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In Situ Bioremediation of Energetic Compounds In Groundwater

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Paul Hatzinger
David Lippincott
Shaw Environmental, Inc.

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14. ABSTRACT
This ESTCP demonstration evaluated the technical effectiveness of in situ bioremediation as a treatment technology for explosives, including RDX, HMX, and TNT, in groundwater at the Picatinny Arsenal in Dover, NJ. A recirculation cell design was employed to distribute and mix cheese whey with contaminated groundwater in order to promote the biodegradation of explosives by indigenous bacteria. The system was operated in a semi-passive mode, such that the whey solution was added to groundwater during active pumping cycles (3-5 days), and then the system was shut down for 6 to 12 weeks. This remedial approach proved to be highly effective for nitramine and nitroaromatic explosives. The applicable regulatory guidance and/or action levels were achieved for RDX and TNT, and there was no significant accumulation of degradation intermediates. Moreover, due to the semi-passive operation, operation and maintenance costs were minimal. The results form this project suggest that in situ bioremediation of explosives in groundwater using semi-passive cosubstrate addition can be a viable long-term treatment approach.

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List of Acronyms and Abbreviations

µg	Microgram(s)
µl	Microliter(s)
µm	Micron(s)
µmols	Micromoles
1,3,5-TNB	1,3,5-Trinitrobenzene
2-ADNT/4-ADNT	2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene,
2,4-DNT/2,6-DNT	2,4- and 2,6-dinitrotoluene
2,4,6-TAT	2,4,6-triaminotoluene
2,6-DANT/2,4-DANT	2, 6-diamino-4-nitrotoluene and 2,4-diamino-6-nitrotoluene
As	Arsenic
bgs	Below ground surface
BHC	Beta-Hexachlorocyclohexane
Br	Bromide
^{o}C	Degrees Celsius
C	Carbon
CH_3CN	Acetonitrile
cm	Centimeter(s)
COC	Chain of Custody
CZMW	Control Zone Monitoring Well
Da	Daltons
DAD	Diode Array Detector
DNB	Dinitrobenzene
DNX	Hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine
DO	Dissolved Oxygen
DoD	Department of Defense
DSERTS	Defense Site Environmental Restoration Tracking System
ECAM	Economic Cost Analysis Methods
EIC	Extracted Ion Chromatogram
EPA/USEPA	United States Environmental Protection Agency
ER	Extraction-Reinjection
ESTCP	Environmental Security Technology Certification Program
ETD	Environmental Technology Division, Picatinny Arsenal
EW	Extraction Well
EVO	Emulsified Vegetable Oil
FBR	Fluidized Bed Reactor
Fe	Iron
ft	Foot/feet
g	Gram

ga	Gauge
GAC	Granulated Activated Carbon
GC	Gas Chromatograph
gpm	Gallons per minute
HA	Health Advisories
HASP	Health & Safety Plan
HCHO	Formaldehyde
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HP	Hydropunch
HPLC	High Performance Liquid Chromatography
HRC	Hydrogen Release Compound
HRT	Hydraulic Retention Time
HSA	Hollow Stem Auger
IDW	Investigation-Derived Waste
IHDIV NSWC	Indian Head Division, Naval Surface Warfare Center
IPR	In Progress Review
ISTW	*In Situ* Treatment Well
IW	Injection Well
K	Hydraulic conductivity
kg	Kilogram(s)
L	Liter(s)
lb	Pound
LC/MS	Liquid-Chromatography-Mass Spectrometry
LHAAP	Longhorn Army Ammunition Plant, Karnack, TX
LOC	Level(s) of Concern
LPH	Liters per hour
m/z	Mass-to-charge ratio
MCGL	Maximum Contaminant Goal Level
MCL	Maximum Contaminant Level
MDL	Method Detection Limits
MEDINA	Methylene dinitramine
MeOH	Methanol
mg	Milligram(s)
min	Minutes
ml	Milliliter(s)
mm	Millimeter(s)
Mn	Manganese
MNX	Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
mS	MilliSiemens
msl	Mean Sea Level

mV	Millivolts
MW	Monitoring Well
N	Nitrogen
NaBr	Sodium Bromide
NB	Nitrobenzene
NA	Not Analyzed
ND	Non-detect
NDAB	4-Nitro-2,4-diazabutanal
NJDEP	New Jersey Department of Environmental Protection
nm	Nanometers
N_2O	Nitrous Oxide
NO_2^-	Nitrite
NO_3^-	Nitrate
NPV	Net Present Value
NRC	National Research Council
NTU	Nephelometric Turbidity Units
O_2	Oxygen
O&M	Operation & Maintenance
OD	Outer Diameter
OLAS	On-line Application System
ORP	Oxidation-Reduction Potential
P&ID	Piping and Instrumentation Diagram
P&T	Pump & Treat
PETN	Pentaerythritol tetranitrate
PI	Principal Investigator
PLC	Programmable Logic Controller
Picatinny	Picatinny Arsenal, Dover, NJ
Picric acid	2,4,6-Trinitrophenol
PLC	Programmable Logic Controller
PQL	Practical Quantitation Limit
PRB	Permeable Reactive Barrier
PVC	Polyvinyl Chloride
QA	Quality Assurance
QC	Quality Control
QAPP	Quality Assurance Project Plan
RCRA	Resource Conservation and Recovery Act
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
SD	Sediment

SERDP	Strategic Environmental Research & Development Program
Shaw	Shaw Environmental and Infrastructure
SO_4^{2-}	Sulfate
SPE	Solid Phase Extraction
SS	Soil samples
STL	Severn Trent Laboratories
SU	Standard Units
SVOC	Semi-Volatile Organic Compound
SW	Surface Water
TDS	Total Dissolved Solids
Tetryl	2,4,6-Trinitrophenylmethylnitramine
TFA	Trifluoroacetic acid
THPS	Tetrakis(hydroxylmethyl)phosphonium sulfate
TIC	Tentatively Identified Compound
TNT	2,4,6-Trinitrotoluene
TNX	Hexahydro-1,3,5-trinitroso-1,3,5-triazine
TOC	Total Organic Carbon
TS	Total Solids
TZMW	Treatment Zone Monitoring Well
USACE	United States Army Corp of Engineers
USGS	United States Geological Survey
UV	Ultraviolet
v	Volume
V	Voltage
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound
wt	Weight
WWI, WWII	World War I, World War II
WWTP	Wastewater Treatment Plant
ZVI	Zero-Valent Iron

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Executive Summary

This ESTCP demonstration evaluated the technical effectiveness of *in situ* bioremediation as a treatment technology for explosives in groundwater at the Picatinny Arsenal in Dover, NJ. A recirculation cell design with semi-passive operation was employed to distribute and mix cosubstrate with contaminated groundwater in order to promote the biodegradation of nitramine and nitroaromatic explosives by indigenous bacteria. Cheese whey was utilized as a cosubstrate during the project based on extensive treatability testing. The overall performance of this design for remediation was determined during the demonstration. The impacts of the technology on the geochemistry of treated groundwater also were evaluated. In addition to technical performance, the demonstration provided the capital and Operations and Maintenance (O&M) costs of this type of system at a scale that can then be extrapolated to different full-scale designs.

This project builds upon recent microbiological research suggesting that explosives-degrading bacteria are widespread, but that they require one or more cosubstrates and anoxic conditions to completely degrade most nitramine and nitroaromatic explosives. The project also applies and tests an engineered groundwater extraction-reinjection (ER) design for cosubstrate mixing with energetics-containing groundwater. To our knowledge, this project represents the first application of an *in situ* semi-passive bioremediation approach for nitramine and nitroaromatic explosives.

During the demonstration, a groundwater ER system was installed to distribute and mix cheese whey as a cosubstrate with explosives-contaminated groundwater in the subsurface. The system, consisting of two extraction wells and a single injection well, was operated in a "semi-passive" mode, pumping for 3-5 days during injection of soluble cheese whey constituents ("active" phase), and then being shut down for 6-12 weeks ("passive" phase) once adequate mixing and distribution of the whey was achieved. The cheese whey was added in four active cycles, beginning on Day 0, Day 41, Day 103 and Day 181 of operation, respectively. A total of 830 kg of cheese whey was added during these cycles (dissolved constituents only) and the system was operated at 10 gallons per minute (gpm) total flow. The final groundwater sampling event was conducted on Day 565 for most sampling parameters, more than a year after the final active cycle. This approach facilitated modification of the aquifer geochemistry to enhance subsurface biodegradation of energetic compounds by indigenous bacteria while minimizing system O&M issues due to biofouling.

The primary performance objective of this demonstration was to reduce explosives in groundwater at Picatinny to concentrations below regulatory concern. For TNT and RDX, the EPA has issued Lifetime Health Advisory Limits (MCGL Values) of 2 μg/L, and the equivalent value for HMX is 400 μg/L. The State of New Jersey Department of Environmental Protection (NJDEP) also issued Interim Groundwater Quality Criteria for

both RDX and TNT in 2008. The specific criteria are 0.3 μg/L and 1 μg/L for RDX and TNT, respectively.

The key performance objective for this demonstration was achieved. Concentrations of TNT in the treatment zone monitoring wells (TZMWs) declined rapidly after cheese whey injection. Initial concentrations ranged from 5 to 190 μg/L during the final baseline sampling event (27 days prior to the first injection beginning on Day 0). The concentration of TNT was below analytical detection limits (PQL = 0.25 μg/L) in all of the TZMWs by Day 62 of the study, and remained at or below this concentration in all TZMWs except one throughout the remainder of the 565-day demonstration. Similar declines in TNT were not observed in upgradient or downgradient control wells (Control Zone Monitoring Wells; CZMWs).

RDX biodegradation occurred somewhat more slowly than for TNT, but 148 days after the initial injection of cheese whey, RDX concentrations were $\leq$ 5 μg/L in all 6 of the TZMWs, and concentrations in 5 of these wells were < 1.5 μg/L. RDX concentrations in the TZMWs ranged from 5 μg/L to 170 μg/L during the final baseline sampling event, with a mean value of 66 μg/L. From Day 222 to Day 565, the concentration of RDX in all of the downgradient TZMWs was < 1 μg/L, and all were < 0.2 μg/L on Day 565. Thus, more than one year after the final injection of cheese whey on Day 181, RDX was < 1 μg/L throughout the downgradient region of the treatment plot. Upgradient TZMWs that were impacted by cheese whey injection also reached < 1 μg/L on Day 148. However, as detailed in the report, the two upgradient TZMWs were not impacted by cheese whey after the initial two injections on Day 0 and Day 41, presumably due to an increased rate of groundwater flow and/or slight shift in groundwater flow direction in the plot area. As the TOC from cheese whey declined in these wells during the study, RDX rebounded in both wells, as expected. In those wells where TOC from cheese whey remained above ~ 5 mg/L throughout the study, rebound was not observed. The data clearly show that cheese whey effectively promoted RDX biodegradation throughout the downgradient treatment zone to concentrations less than Federal MCGL values and New Jersey interim action levels, and that as long as a minimal concentration of TOC is maintained, rebound is unlikely.

The HMX concentration in the TZMWs wells ranged from 3.5 to 130 μg/L (mean value 50 μg/L) during the final baseline sampling event. Thus, all wells had baseline concentrations below the EPA MCGL of 400 μg/L. However, a significant decline in HMX was observed in all wells, and by Day 274, each of the 4 downgradient TZMWs had HMX concentrations < 0.4 μg/L. A slight rebound was observed in one downgradient TZMW on Day 565, but HMX remained < 1 μg/L in each of the other wells throughout the remainder of the study. Thus, as with RDX and TNT, the data from the downgradient TZMWs indicate that the addition of cheese whey to the Picatinny aquifer effectively promoted HMX biodegradation to sub μg/L concentrations. Moreover, as long as TOC concentrations were maintained > 5 mg/L, rebound of HMX was not observed.

A number of other nitroaromatic compounds also were quantified throughout the demonstration, including several nitrobenzenes and nitrotoluenes, 2,4,6-trinitrophenol (picric acid), 2,4,6-trinitrophenylmethylnitramine (Tetryl), and pentaerythritol tetranitrate (PETN). Among these compounds, 1,3,5-trinitrobenzene (1,3,5-TNB) was present throughout the demonstration plot at ~ 10 to 70 μg/L prior to cheese whey injection. A rapid decline in the concentrations of this compound was observed in all TZMWs (< 0.25 μg/L by Day 62) and the concentration remained < 0.6 μg/L in all TZMWs until the final samples for this compound were collected on Day 420. Similar declines were not observed in CZMWs with this compound.

Among the other compounds detected in the treatment plot, 2,4-dinotrotoluene (2,4-DNT) and 2,6-dinotrotoluene (2,6-DNT) also were biologically degraded in the treatment zone wells. 2,4-DNT was detected consistently in several wells during baseline sampling at concentrations ranging from ~ 0.5 to 1.7 μg/ L (0.25 μg/L PQL). The compound was not detected in any of the other wells, except the extraction wells during system operation. After cheese whey addition, 2,4-DNT declined to <0.25 μg/L in the TZMWs by Day 33, and with a few exceptions, remained below this concentration throughout the demonstration. Similar results were observed for 2,6-DNT in the same wells.

Another critical performance objective for this demonstration was to show that there was no long-term accumulation of common daughter products of TNT or RDX biodegradation under anoxic conditions. This performance objective also was met during the study. Two common TNT daughter products, 4-amino-4,6-dinitrotoluene (4-ADNT) and 2-amino-2,6-dinitrotoluene (2-ADNT) were present from ~ 1 to 120 μg/L in groundwater monitoring wells at the demonstration site during baseline sampling. These products are formed from an initial reduction of one nitro-group on TNT to an amino group, and may either have been present in the water released from the facility during processing, or have formed after disposal to land surface via biological reactions. A rapid reduction in the concentrations of both of these compounds in groundwater was observed following injection of cheese whey. In fact, neither TNT daughter product was present above the analytical PQL of 0.25 μg/L in the TZMWs by Day 148. There was a slight rebound of these compounds in upgradient wells after this time, but each of these wells was not impacted by cheese whey after the initial injection, as previously discussed. For each of the other TZMWs, concentrations of these compounds remained below detection (< 0.25 μg/L) from Day 148 to the final sampling event. There was no appreciable increase or decrease in the concentration of these compounds in the wells outside of the treatment zone.

With the exception of one detection, 2,4-diamino-6-nitrotoluene (2,4-DANT) and 2,6-diamino-4-nitrotoluene (2,4-DANT) were not present in Picatinny groundwater prior to cheese whey injection. These compounds, each of which is an expected degradation intermediate of TNT, increased in the TZMWs as TNT biodegraded and then declined in

concentration to below their respective PQL values by Day 98 and for the duration of the demonstration in all downgradient TZMWs**.**

The concentrations of the common RDX daughter products MNX, DNX, and TNX increased in one or more of the TZMWs as biodegradation proceeded. However, the total concentrations were < 20 μg/L in all cases, and generally much lower, and all three nitroso-derivatives were transient. The production of these intermediates is expected during reductive biodegradation of the nitramine, and clearly indicates that the explosive is being biologically reduced in the treatment area wells. A significant decrease in the concentrations of each of these daughter products was observed during the demonstration, and all were near or below detection by Day 420 of groundwater monitoring. All three products remained below detection in wells sampled on Day 565. Overall, the data suggest that each of the RDX nitroso-derivatives were further biodegraded in the aquifer.

Microbial biofouling is a significant concern with any *in situ* remedial system, and particularly with those requiring active pumping. During this demonstration, techniques to control biofouling included: (1) pumping groundwater intermittently rather than continuously, and reducing the active pumping phase as much as possible, (2) injecting large quantities of cosubstrate during the pumping phase; and (3) injecting groundwater through a pressurized packer to promote movement of water into the formation. Significant pressure increases were not observed in the injection well during the four pumping phases, so additional control or well rehabilitation measures were not necessary. Most importantly, using the pumping design primarily as a means to mix cosubstrate into the aquifer was determined to significantly reduce the potential for biofouling and the associated costs with this issue.

During the demonstration, reasonably high concentrations of Fe, Mn, and methane were observed in some of the monitoring wells. Fe and Mn exceeded 40 mg/L in some of the central wells and methane exceeded 10 mg/L. Because this was largely a source zone treatment application, and groundwater transport was slow, it was not possible during the timeframe of the study to assess whether these compounds were still present in the furthest downgradient monitoring wells because the treated water did not reach these wells during the course of the study. However, one of the reasons for the relatively high concentration of these compounds during this study was the application of cheese whey rather than a single carbon substrate. In addition, relatively high concentrations of whey were added at each injection cycle so that the number of cycles could be minimized. This approach proved to be highly effective for remediation of explosives and degradation intermediates over the 565-day study, and no significant operational issues were experienced, such as well fouling. However, one trade-off for this approach was the production/mobilization of some secondary groundwater contaminants, such as Fe, Mn and methane. Because there were no drinking wells in the local area and no close downgradient receptors, these contaminants were not deemed to be an important issue.

However, mobilization of such contaminants should be considered in cases where downgradient receptors are present, and system operation and carbon sources should be chosen or adjusted accordingly.

Overall, this *in situ* bioremediation approach proved to be highly effective for the treatment of nitramine and nitroaromatic explosives in groundwater. The applicable regulatory guidance and/or action levels were achieved for RDX and TNT, there was no significant accumulation of degradation intermediates, and the active-passive treatment approach resulted in no significant O&M issues. Moreover, after only four active injection cycles, concentrations of total organic carbon (TOC) from the cheese whey remained high enough in downgradient monitoring wells to promote degradation of explosives and intermediates for more than a year after the final injection. The data showed that as long as TOC concentrations greater than ~ 5 mg/L were maintained rebound of explosives was negligible. Thus, this project clearly shows that *in situ* bioremediation of explosives in groundwater using active-passive cosubstrate addition can be a viable long-term treatment approach. This technology is expected to be widely applicable at military installations across the United States.

1.0 INTRODUCTION

This ESTCP project was a collaborative effort among scientists at Shaw Environmental Inc., (Shaw; Lawrenceville and Mt. Arlington, NJ Offices), the NRC Biotechnology Research Institute (Montreal, Canada) and the Environmental Technology Division (ETD) at Picatinny Arsenal in Dover, NJ (Picatinny). The objective of this project was to demonstrate *in situ* bioremediation of energetic compounds in a contaminated aquifer using cosubstrate addition to stimulate indigenous bacteria capable of degrading these explosives. The demonstration project was performed at a former explosives packing facility (Area 157) at Picatinny. A groundwater recirculation system was installed to distribute and mix cheese whey as a cosubstrate with explosive-contaminated groundwater in the subsurface. The system was operated in a "semi-passive" mode, pumping for 3-5 days during injection of liquid cheese whey (active phase), and then being shut down for 6-12 weeks (passive phase) once adequate mixing and distribution of the whey was achieved. This approach facilitated modification of the aquifer geochemistry to enhance subsurface biodegradation of energetic compounds by indigenous bacteria while minimizing system Operations and Maintenance (O&M) issues due to biofouling. The data suggest that bioremediation can be used effectively in groundwater to treat common energetic compounds, including TNT, RDX, and HMX. This approach is expected to be widely applicable for *in situ* remediation of these compounds at DoD sites.

1.1 Background

The energetic compounds, 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and various breakdown products from these materials, such as 2,4- and 2,6-dinitrotoluene (2,4-DNT, 2,6-DNT) are widespread soil contaminants at many current and former military facilities. Because these compounds can be transported through soils to the subsurface, they are now also impacting groundwater and drinking water at numerous locations across the country. According to a recent report from the U.S. Army Corps of Engineers, the U.S. Army has 583 sites at 82 installations that have explosives contamination in groundwater, and 87 additional locations with suspected contamination (Wani et al., 2003). Picatinny has several sites in with explosives in soils and groundwater (Picatinny Arsenal, 2001).

1.1.1 TNT Biodegradation

The capacity to degrade explosive compounds appears to be reasonably widespread across bacterial genera (Fuller and Manning, 1997). The biological degradation of TNT by bacteria and fungi has been extensively studied (e.g., Alvarez et al., 1995; Bayman and Radkar, 1997; Boopathy et al., 1993; 1994a,b; Spain et al. 2000). The biodegradation of TNT and other munitions compounds by most bacterial species appears to be a cometabolic process in which the extent of TNT degradation is dependent upon

the type and concentration of a cosubstrate. Cosubstrates, including glucose (Preuβ et al., 1993), acetate (Boopathy et al., 1993; 1994a), succinate (Boopathy et al, 1994b), molasses (Fuller and Manning, 1997; Manning et al., 1995; Widrig et al., 1997), and potato starch (Funk et al., 1993), have been used in laboratory studies to support the biological transformation of munitions. Solid substrates used in composting, such as manure, alfalfa, and horse feed, have also been shown to support the biological degradation of TNT (Kaplan and Kaplan, 1982; Williams et al., 1992). During the biotransformation of TNT, one or two of the nitro groups are initially reduced to nitroso (-NO), hydroxylamino (-NHOH), and then amino ($-NH_2$) functionalities, respectively (Hawari et al., 2000a). This reductive pathway has been shown to occur in many environments, including soils, waters, sewage, and compost (Walker and Kaplan, 1992). Common biotransformation products of TNT are reduced amino compounds, including 4-amino-2,6-dinitrotoluene (4-ADNT), 2-amino-4,6-dinitrotoluene (2-ADNT), 2,6-diamino-4-nitrotoluene (2,6-DANT) , 2,4-diamino-6-nitrotoluene (2,4-DANT), and 2,4,6-triaminotoluene (2,4,6-TAT). The microbial degradation of TNT often does not progress to a point where the ring structure is opened and products are converted to carbon dioxide (i.e., mineralization). However, the amino derivatives bind strongly to organic solids and clays, and this sorption can be irreversible. These compounds, or other partially reduced derivatives (e.g., nitroso or hydroxylamino derivatives) also can polymerize with each other and with other organic compounds, producing polymers with low solubility and toxicity (Pennington et al., 1997). Thus, one effective strategy to prevent migration of TNT to groundwater is biological reduction and subsequent binding of reduced TNT derivatives.

1.1.2 RDX and HMX Biodegradation

The biological degradation of the nitramine explosives RDX and HMX has been less exhaustively studied than for TNT. However, research has demonstrated that both of these compounds can be degraded by bacteria (McCormick et al., 1981; Boopathy and Manning, 2000; Harkins et al., 1999; Hawari et al., 2000a,b; Kitts et al., 1994, 2000; Shen et al., 2000). The biodegradation of RDX has been observed under both anoxic and aerobic conditions **(Figure 1.1** and **Figure 1.2)**. The biodegradation pathway for RDX under anoxic conditions has been shown to proceed by sequential reduction of the nitro groups to nitroso groups, resulting in the formation of hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) **(Figure 1.1A)**. This compound is then reduced further to hydroxylamine derivatives, after which ring cleavage occurs, resulting in the formation of various products, including formaldehyde, nitrous oxide, methanol, and carbon dioxide (Hawari et al., 2000a,b; 2002). A second anaerobic pathway has been identified that proceeds via initial denitration and direct ring cleavage of RDX to form methylene dinitramine (MEDINA) and bis(hydroxymethyl)nitramine; these compounds subsequently breakdown further to nitramine, formaldehyde and nitrous oxide **(Figure 1B)**. The anaerobic degradation of RDX often requires an organic (or inorganic) cosubstrate to proceed, much like TNT. In some instances, RDX has been proposed to serve as an alternate electron acceptor for bacteria under anaerobic conditions (e.g.,

Beller, 2002), while in other cases, RDX appears to serve as a microbial nitrogen source (Boopathy et al., 1998; Coleman et al., 1998). Within diverse microbial communities, RDX and/or its degradative intermediates may serve both purposes for some bacteria, and may provide carbon and energy to some strains as well. The disposition of C and N from this molecule within microbial communities is currently the subject of extensive research (e.g., SERDP Project ER-1607).

RDX has also been shown to be biodegradable by select microbial isolates under aerobic conditions, and has generally been hypothesized to serve as a N source to these strains (Binks et al., 1995; Coleman et al., 1998; Sheremata and Hawari, 2000; Seth-Smith et al., 2002, 2008; Fournier et al., 2002) or for two organisms (*Williamsia* sp. KTR4 and *Gordonia* sp. KTR9), a sole source of both nitrogen and carbon (Thompson et al., 2005). The proposed aerobic pathway of microbial degradation of RDX occurs through two initial enzymatic denitration steps that result in the release of nitrite and the spontaneous decomposition of RDX in water to form 4-nitro-2,4-diazabutanal (NDAB) and formamide (**Figure 1.2**; Fournier et al., 2002; Bhushan et al., 2003). The Cytochrome P450 isozyme CYP177A1, XplA (XplA) has been identified as the key enzyme system in the aerobic degradation of RDX (Seth-Smith et al., 2002, 2008; Jackson et al., 2007). HMX can also be biodegraded aerobically by the fungus *Phanerochaete chrysosporium* (Fournier et al., 2004).

Whether or not RDX and HMX are biodegraded under aerobic conditions in natural environments, including groundwater aquifers, is still unclear. Current research in our laboratory with samples from several different RDX-contaminated aquifers has revealed no significant aerobic biodegradation potential, whereas the nitramine is usually biodegraded anaerobically when a suitable carbon substrate is added to site samples (*unpublished data*, Fuller and Hatzinger, 2012). Moreover, NDAB has rarely been observed at aerobic groundwater sites with RDX, despite the fact that this intermediate is relatively stable in water. Thus, it appears that aerobic mineralization of RDX and HMX is possible, but the extent to which this will occur in natural environments, including soils and groundwater, is unknown.

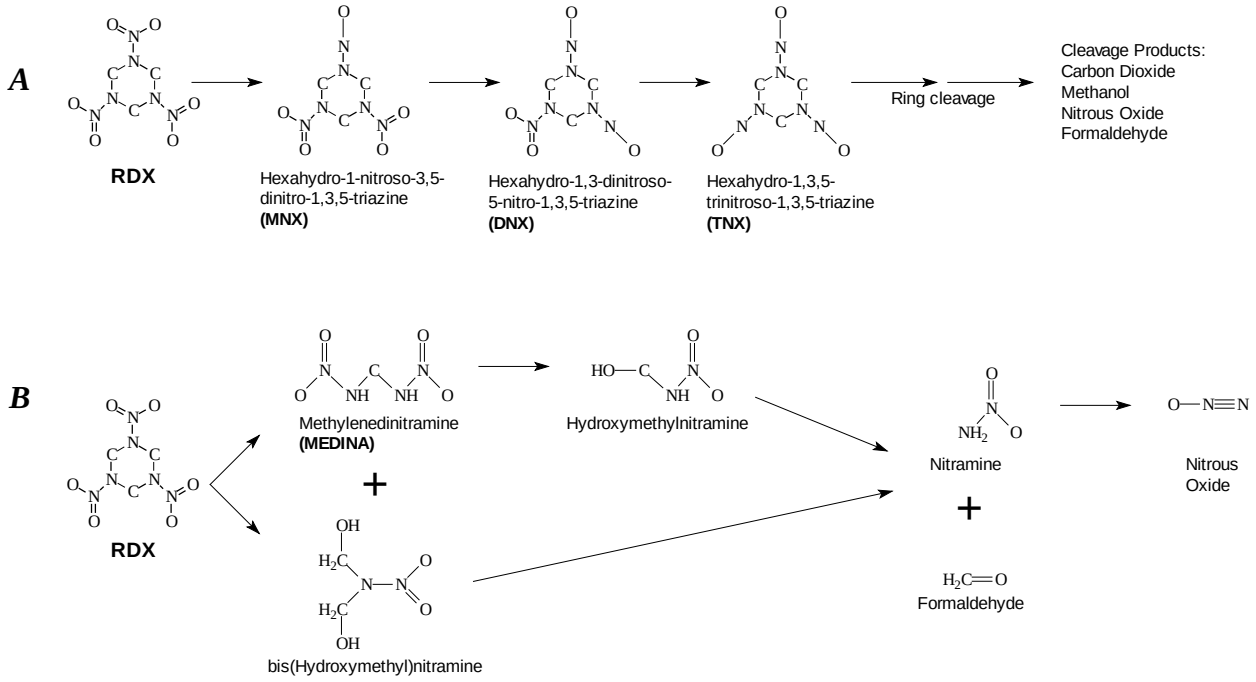

Figure 1.1. Pathways of RDX biodegradation under anoxic conditions.

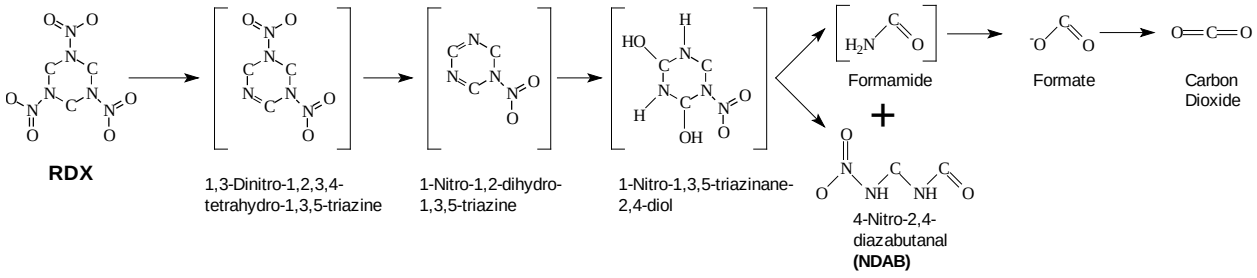

Figure 1.2. Pathway of RDX biodegradation under aerobic conditions.

1.1.3 Bioremediation of Explosives in Groundwater

A variety of different systems have been tested to promote *in situ* and *ex situ* bioremediation of these explosives in soils using substrate addition (Pennington, et al., 1995; Boopathy and Manning, 1998; Widrig et al., 1997; Fuller et al., 2003). Unlike soils, however, efficient and cost-effective bioremediation technologies for groundwater containing explosives are very limited. The current methodologies for contaminated groundwater, which include granulated activated carbon filtration (GAC) (Bricka and Sharp, 1993) and UV-oxidation (Bricka and Sharp, 1993) are either ineffective, or very expensive for water treatment. In addition, the bioremediation technologies that are applicable for remediation of concentrated explosives (mg/kg to g/kg levels) in soils are not applicable for groundwater, where low contaminant concentrations (μg/L to mg/L) are likely to be present in large plumes.

Laboratory experiments conducted during SERDP Project CU-1163 revealed the potential for combined treatment of perchlorate and RDX by naturally-occurring bacteria in subsurface environments (Envirogen, 2002). **Figure 1.3** shows the degradation of RDX in flow-through columns prepared using aquifer solids from the Longhorn Army Ammunition Plant (LHAAP). Lactate was fed as a cosubstrate during these studies. Similar column studies were also conducted with aquifer solids and groundwater from the Nebraska Ordnance Plant (Wani and Davis, 2003; Davis et al., 2004). In these experiments, several different cosubstrates (including ethanol, acetate, and soluble starch) were observed to facilitate RDX biodegradation from influent levels of ~100 μg/L to < 1 μg/L with a 27.5 hr residence time. Schaefer et al., (2007), also recently reported the biodegradation of RDX and HMX in aquifer samples from a military site in MD, using an emulsified oil substrate to promote biological activity. Thus, laboratory data clearly show the potential for *in situ* bioremediation of explosive compounds in groundwater.

In addition to laboratory studies of *in situ* treatment options, Other reports have also shown that both HMX and RDX can be mineralized to carbon dioxide under anoxic conditions in slurry reactors (Shen et al., 1998a,b, 2000; Young et al., 1997). In addition, a recent pilot study using contaminated groundwater from a military installation revealed that perchlorate, RDX, and HMX can be jointly biodegraded in acetate-fed fluidized bed reactors (FBRs) to effluent levels below regulatory requirements (Fuller et al., 2007). These data, combined with data from other research projects on explosives degradation, support the development of an *in situ* biotreatment technology to remediate groundwater contaminated with energetic compounds. An *in situ* biological treatment regime offers the best possibility for efficient and cost effective remediation of explosive compounds-contaminated groundwater. This technology is expected to be widely applicable at military installations across the United States.

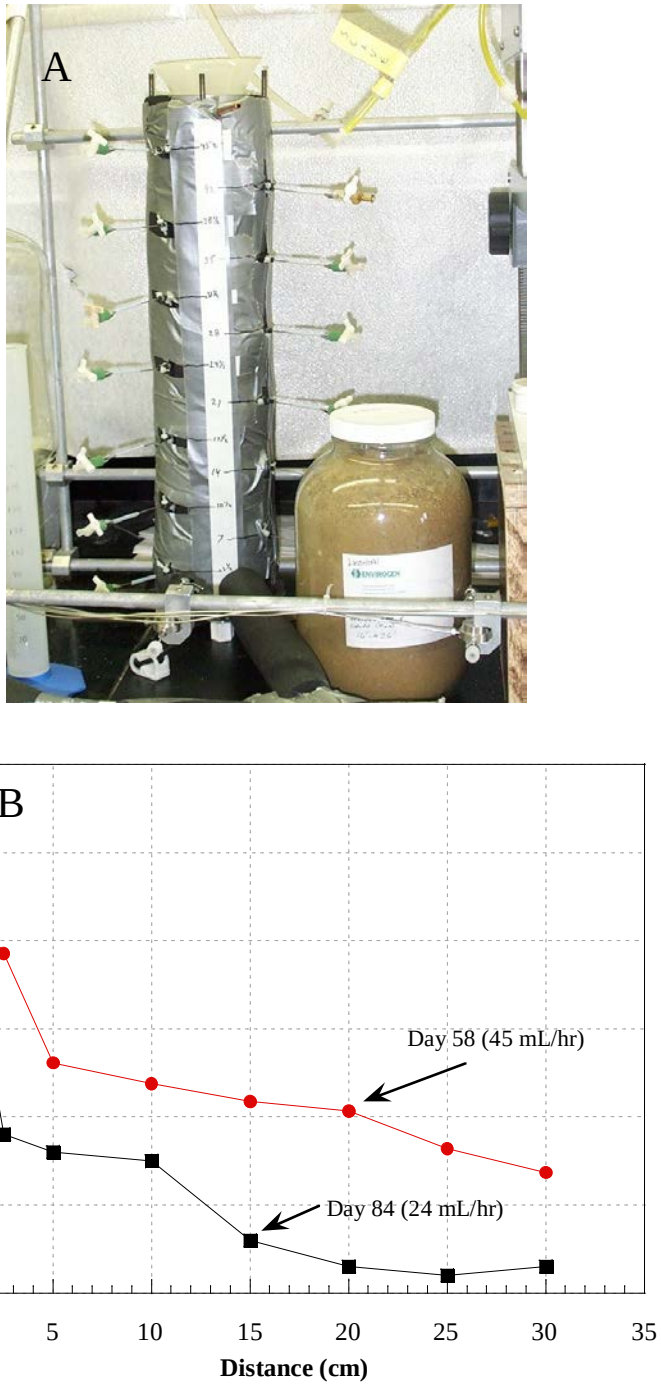

Figure 1.3. Degradation of RDX in a 30-cm flow-through model aquifer containing sediment from the Longhorn Army Ammunition Plant. The column with sampling ports is shown in (A) and the RDX data from each sampling port at two different times (Day 58 and Day 84) is shown in (B).

1.2 Objectives of the Demonstration

This project was designed to test and validate the following: (1) *in situ* anoxic bioremediation of energetics-contaminated groundwater through cosubstrate addition, and (2) the application of a "semi-passive" groundwater extraction-reinjection (ER) system to achieve mixing of the cosubstrate with the explosives-contaminated water, and delivery of the mixture to indigenous explosives-degrading bacteria. One key was to demonstrate that cosubstrate addition can be used to efficiently and cost-effectively treat energetic compounds in subsurface groundwater to below levels of regulatory concern. One of the most critical issues in applying an organic cosubstrate or other amendment to the subsurface is how to facilitate mixing of that chemical with contaminated groundwater. If sufficient mixing is not achieved, areas of untreated water will pass through the treatment zone, and the technology will be ineffective as a long-term remedy. The creation of a recirculation cell within a subsurface aquifer using an engineered groundwater extraction-reinjection system helps to ensure proper mixing and delivery of cosubstrate at required concentrations. The semi-passive operation of this system is subsequently utilized to reduce O&M costs.

The semi-passive operation occurs as follows. During "active" treatment, the ER system removes contaminated groundwater from an aquifer via extraction wells. The extracted groundwater is then amended with the chosen cosubstrate, and re-injected into one or more injection wells. The active phase generally occurs for a few days to a few weeks until the cosubstrate is adequately distributed in the aquifer. The ER system is subsequently shut down for weeks to months during the "passive" phase, during which time biodegradation occurs within the aquifer. The key advantage of a semi-passive approach compared to either a completely passive system (e.g., vegetable oil injection) or a completely active system, is the ability to effectively distribute cosubstrate while minimizing O&M issues (such as well biofouling) associated with continuous active pumping approaches. More information on active, passive, and semi-passive approaches is available in Stroo and Ward, 2009.

1.3 Regulatory Drivers

There is currently no federal drinking water standard (maximum contaminant level [MCL]) for the nitroaromatic and nitramine explosives that are the object of this demonstration. However, the U.S. Environmental Protection Agency (USEPA) has listed RDX and 2,4- and 2,6-dinitrotoluene (2,4-DNT, 2,6-DNT) – two breakdown products of TNT – on both the Draft Drinking Water Candidate Contaminant List and the Unregulated Contaminant Monitoring Regulation List (Federal Register, 1999). In addition, the EPA has issued lifetime Health Advisory Limits (Maximum Contaminant Goal Levels; MCGL) of 2 μg/L for RDX and TNT, and 400 μg/L for HMX (US EPA, 2004).

The State of New Jersey Department of Environmental Protection (NJDEP) has also issued Interim Groundwater Quality Criteria for both RDX and TNT in 2008 (NJAC,

2010). The specific criteria are 0.5 μg/L for RDX and 1 μg/L for TNT (see **Table 1.1** for all NJ Groundwater Criteria). The New Jersey Groundwater Quality Criteria are designed to protect public health in drinking water aquifers.

Table 1.1. New Jersey Interim Ground Water Quality Criteria in Parts Per Billion (μg/L).
Values from the New Jersey Department of Environmental Protection.

Constituent	CASRN	Interim GWQ Criterion	PQL	Higher of PQL and Interim GWQC	Effective Date	Support Documents
acenapthylene	208-96-8	100*	10	100	11/7/05	DEP, 9/04
acetonitrile	75-05-8	100*	9	100*	2/11/08	DEP, 2/08
benzo(g,h,i)perylene	191-24-2	100*	0.3	100	11/7/05	DEP, 9/04
caprolactam	105-60-2	3500	5000	5000	2/11/08	DEP, 2/08
4-chloro-3-methylphenol	59-50-7	100*	20	100	11/7/05	DEP, 9/04
chloroethane	75-00-3	5*	0.5	5*	2/11/08	DEP, 2/08
cobalt	7440-48-4	100	0.5	100	2/11/08	DEP, 2/08
dichlormid	37764-25-3	600	50	600	2/11/08	DEP, 2/08
dimethyl phthalate	131-11-3	100	10	100	11/7/05	DEP, 9/04
4,6-dinitro-o-cresol	534-52-1	0.7	1	1	2/11/08	DEP, 2/08
1,4-dioxane	123-91-1	3	10	10	2/11/08	DEP, 2/08
diphenyl ether	101-84-8	100	10	100	2/11/08	DEP, 2/08
2-ethyl-1-hexanol	104-76-7	200	0.5	200	2/11/08	DEP, 2/08
n-heptane	142-82-5	100*	0.5	100*	2/11/08	DEP, 2/08
hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4	0.3	0.5	0.5	2/11/08	DEP, 2/08
2-hexanone	591-78-6	300	1	300	2/11/08	DEP, 2/08
metolachlor	51218-45-2	100	0.5	100	2/11/08	DEP, 2/08
2-(2-methyl-4-chlorophenoxy) propionic acid (MCCP)	93-65-2	7	0.5	7	2/11/08	DEP, 2/08
2-methylnapthalene	91-57-6	30	10	30	2/11/08	DEP, 2/08
n-propanol	71-23-8	100*	40	100*	2/11/08	DEP, 2/08
perchlorate	14797-73-0	5	2.7	5	3/26/07	DWQI, 10/7/05
phenanthrene	85-01-8	100*	0.3	100	11/7/05	DEP, 9/04
2,4,6-trinitrolouene (TNT)	118-96-7	1	0.3	1	2/11/08	DEP, 2/08

***Note:** All interim criteria identified on this table are **interim specific** ground water quality criteria unless noted with an asterisk (*), which indicates that they are **interim generic** ground water quality criteria.

2.0 TECHNOLOGY

2.1 Technology Description

This project builds upon recent microbiological research suggesting that explosives-degrading bacteria are widespread, but that they require selected cosubstrates and anoxic conditions to completely degrade most nitramine and nitroaromatic explosives (see *Introduction* for references). The project also applies and tests an engineered groundwater recirculation design for cosubstrate mixing with energetic-containing water. This system was operated in a semi-passive mode to provide mixing of cosubstrate with groundwater while minimizing typical O&M issues (e.g., well biofouling, well redevelopment) associated with continuously active pumping approaches. Similar extraction-reinjection (ER) designs were shown to be highly effective for *in situ* treatment of perchlorate at Indian Head Division, Naval Surface Warfare Center (IHDIV NSWC) in Maryland (Hatzinger et al., 2006) and at the Longhorn Army Ammunition Plant (LHAAP) in Karnack, TX (Krug and Cox, 2009). To our knowledge, this project represents the first application of a semi-passive ER approach for nitramine and nitroaromatic explosives. This technology is anticipated to be widely applicable at DoD sites containing explosives, or a mixture of explosives and propellants in groundwater.

The demonstration project was performed at the Picatinny Arsenal in Dover, NJ (Picatinny) (see Section 4). A site investigation at Picatinny revealed that several shallow monitoring wells near former explosives production areas contain energetic compounds, including HMX, RDX, and TNT. The energetic apparently migrated from the surface soils to the sandy, unconsolidated aquifer by leaching and infiltration, resulting in groundwater contamination. Two major plume areas of explosive compound migration have been identified (Group I Sites; Areas 40 and 157, respectively). The Area 157 plume was selected for the demonstration based on contaminant concentrations, hydrogeological considerations, and site access as described in Section 4.

A groundwater recirculation design was used to distribute and mix cosubstrate with explosives-contaminated groundwater and to deliver that substrate to indigenous bacteria **(Figure 2.1** and **Figure 2.2)**. The recirculation design consisted of two groundwater extraction wells and one groundwater injection well installed in the aquifer cross-gradient to groundwater flow. A general schematic of the recirculation design is provided in **Figure 2.1.** The details of the system design and operation are described in more detail in Sections 5.3 and 5.4. The groundwater was removed from the aquifer through the two extraction wells, amended with cheese whey as a cosubstrate at the surface, and then reinjected into the formation through the single injection well. The injection well included a packer near the water table surface to allow injection of water under moderate pressure, and a variable speed pump which was used to mix the cosubstrate-amended groundwater within the well. This pump was also available to mix biofouling control agent with groundwater in the well, although that process was not necessary based on well pressures. The operation of this system provided mixing of the cosubstrate with the

explosives-contaminated groundwater and created a subsurface recirculation zone between the two extraction wells and the injection well. The operating conditions for the system, including pumping rates, pumping schedule (i.e., the system ran intermittently), and cosubstrate injection parameters, were readily controlled and easily modified. The initial system design and operational conditions for the demonstration were based on results from a site specific reactive transport model developed for the project (see Section 5.2.6 and **Appendix C**).

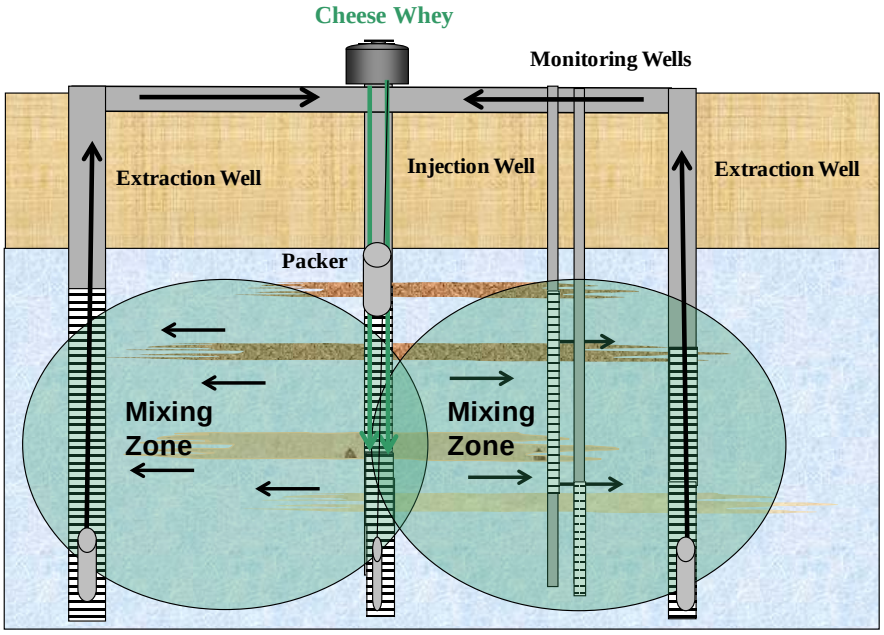

Figure 2.1. Schematic of extraction-reinjection design.

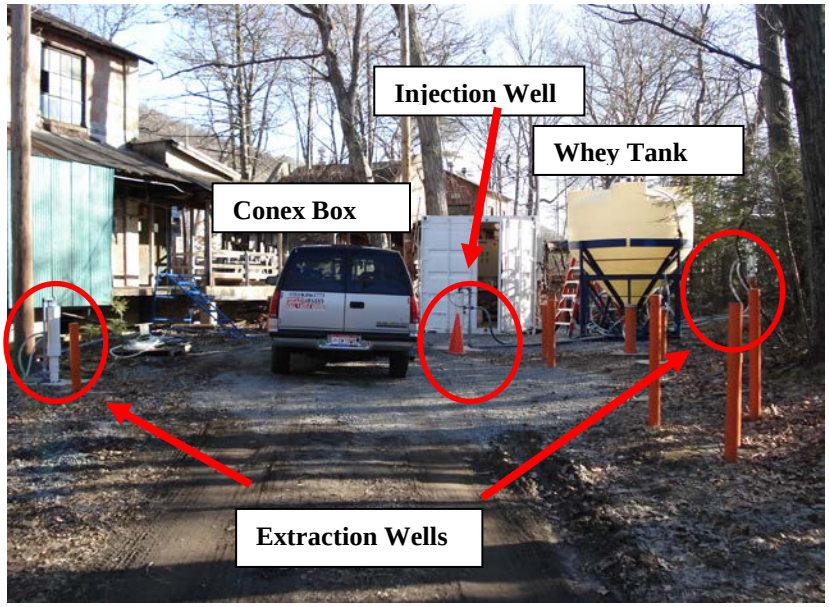

Figure 2.2. Photograph of the demonstration site.

A total of 9 monitoring wells (including 3 nested wells) were used to evaluate the success of the demonstration (see **Figure 2.3** for well layout). Four of these wells (157MW-1 to 157MW-4) were installed previously during investigative work in the Group 1 area. Well 157MW-5 was installed for this project as part of the initial site assessment work and to collect core samples for laboratory studies. The remaining nested wells (157MW-6S/6D, 157MW-7S/7D and 157MW-8S/8D) were installed in two phases. Nested wells 157MW-6S/6D were installed first and used for a pump testing as described in Section 5.2.5. The remaining two pairs of nested wells were installed later. Their location and screen intervals were based on the pump test and other site assessment results as described in Section 5.2. The extraction (2) and injection wells (1) were installed at the same time as the final set of monitoring wells. One additional deep bedrock well (157MW-1D) was also sampled throughout the demonstration although it was anticipated to be screened well below the zone of influence of the treatment system, and contained only trace concentrations of explosives (i.e., < 2 μg/L). A Conex box was designed to house the metering pumps, controls, and electrical equipment necessary to control the extraction and injection well pumps and to facilitate the amendment of groundwater with appropriate cosubstrate and biofouling control agents (see **Figure 2.2**).

The key design criteria for this type of system include the following: (1) the location, size, and screen intervals of extraction and injection wells; (2) the system pumping rates and pumping schedule (i.e., passive vs. active phases), (3) the cosubstrate type, concentration, and dosing regimen; and (4) operational measures to minimize well biofouling. The location of the pumping wells and the pumping rate and schedule were determined using a site-specific reactive transport model. In turn, the parameters for this model were based on the measured hydrogeological conditions at the site, the concentration and extent of contamination requiring treatment, and the estimated rates of contaminant degradation derived from laboratory microcosms and column studies. A groundwater fate and transport model was developed for this site based on hydrogeological data (geology, hydraulic gradient, hydraulic conductivity, etc), contaminant concentrations, and estimated degradation rates from site-specific microcosm studies (see Section 5.2.6 & **Appendix C**). This model was used to select locations for the injection well, extraction wells, and monitoring wells, and to evaluate different operating scenarios.

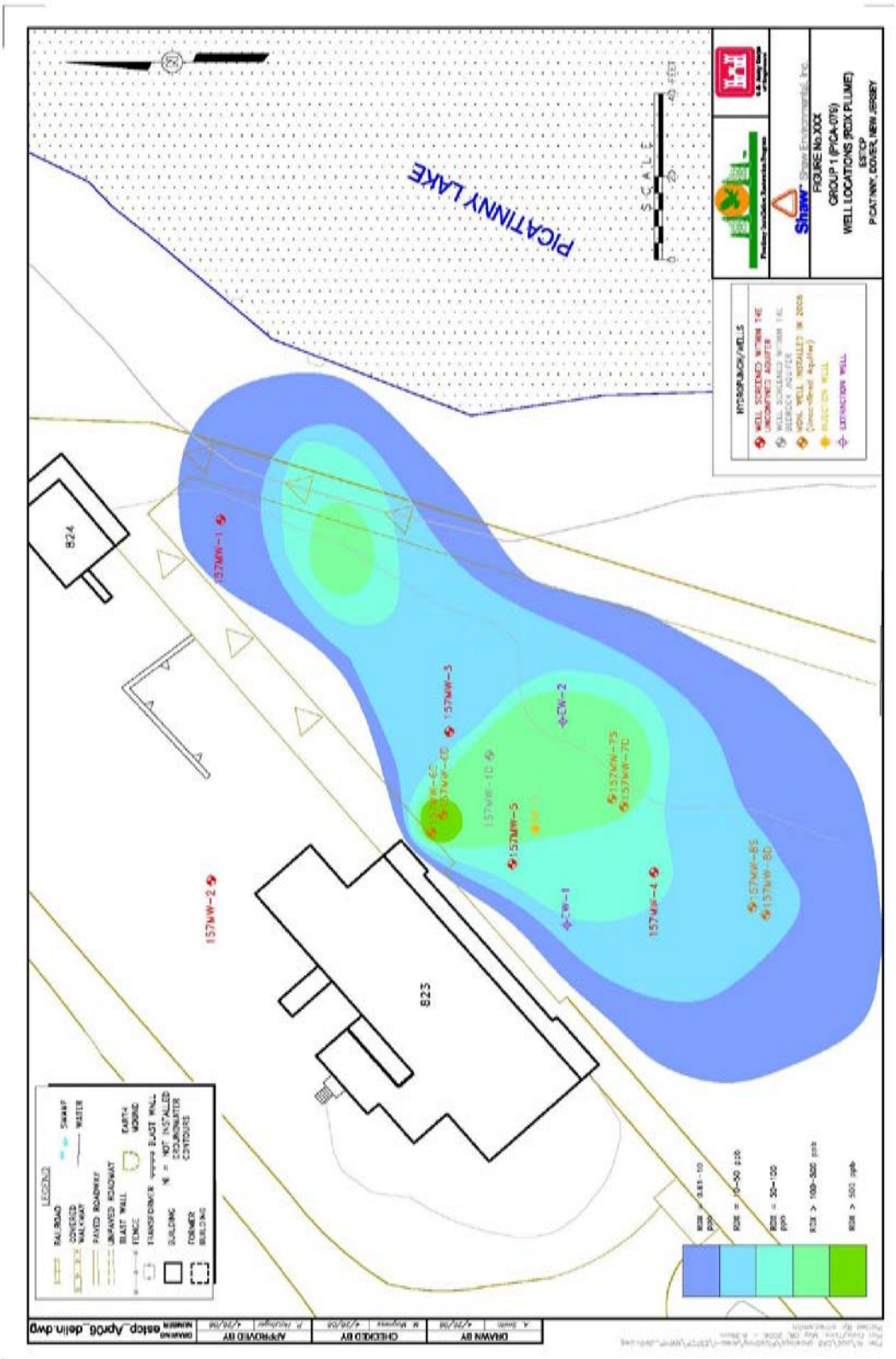

Figure 2.3 Layout of the demonstration plot. The RDX plume map is shown with the well locations.

There are many potential applications for the groundwater recirculation and mixing design that was demonstrated; from treatment of source areas or diffuse plumes, to cut-off an expansive plume. In addition, this approach can potentially be applied for treatment of a variety of contaminants, including explosives, such as RDX, HMX, TNT and explosives breakdown products (e.g., MNX, DNX, 2,4-DNT, 2,6-DNT), perchlorate, nitrate, various redox-sensitive metals (including uranium, selenium, vanadium, and chromium), and chlorinated solvents. The key advantages of this design are as follows: (1) the system can be used to create hydraulic control (if run continuously or semi-continuously); (2) the substrate and groundwater can be thoroughly mixed allowing general control of redox conditions; and (3) the operational parameters of the system, including cosubstrate type and concentration, pumping rates, pumping schedule, etc., can be controlled and modified based on performance.

For *in situ* treatment, the primary alternative to this system is the passive injection of a cosubstrate, either a soluble substrate or a slow-release material. This approach does not provide any hydraulic control or containment, relies on groundwater flow for distribution and total treatment area, and once applied, cannot be modified (i.e., vegetable oil cannot easily be removed once injected). However, the passive approach is generally much simpler in design than the recirculation cell, requires less hydrogeologic and geochemical data, and is not prone to the operational issues of an active pumping system, including well maintenance issues. A thorough evaluation of different approaches to amend aquifers with substrates is provided in Stroo and Ward, (2009).

2.2 Technology Development

At present, there is very little information in the literature on pilot or full-scale demonstrations of biostimulation for *in situ* explosives treatment in groundwater. Much of the *in situ* remedial work to date with these compounds has focused on approaches for contaminated soils. However, significant laboratory data support the potential for *in situ* treatment of explosives by indigenous organisms through addition of different cosubstrates (see *Section* 1.1.3 for discussion and references). The development of a semi-passive approach for groundwater treatment has evolved in large part from operational issues associated with active pumping systems, and in particular, well biofouling issues. A discussion of O&M associated with active systems is provided in Hatzinger et al., (2009). An active system is perhaps the best way to effectively inject and mix substrates into groundwater, in addition to providing hydraulic control at a site. However, technical and cost issues associated with biofouling of injection wells in active systems remain a significant detriment to the widespread application of this approach.

The semi-passive treatment approach potentially provides many of the benefits of active treatment, including effective distribution of a soluble carbon source, minimization of secondary impacts to groundwater quality associated with slow-release carbon sources (e.g., vegetable oil), and flexibility in design and operation, but has less overall potential

for biofouling issues due to the very limited time of operation of the extraction and reinjection wells.

The development of a semi-passive pumping approach was initially proposed in the early 1990's as a potential mechanism to introduce required "nutrients" for enhancing pollutant bioremediation within a permeable barrier wall design while reducing O&M issues associated with constant pumping (Devlin and Barker, 1994). The approach was subsequently tested at the Canadian Forces Base site in Borden, Ontario as a means to inject and distribute potassium acetate into groundwater via a "nutrient injection wall" (Devlin and Barker, 1999). The data from this study suggested that a pulsed injection could be used to introduce solutes uniformly within an aquifer (i.e., during the pumping phase) with only minimal impact to normal groundwater flow in the passive phase. This research group subsequently tested a semi-passive approach for *in situ* treatment of mixed chlorinated solvents using benzoate as an electron donor (Devlin et al. 2004) and then for nitrate in a drinking water aquifer near a municipal supply well (Gierczak et al., 2007). Both tests were successful, and pulsed addition of stoichiometric quantities of carbon source (acetate) in the second field test allowed reduction of nitrate to occur without significant production of nitrite or reduction of sulfate.

At least two perchlorate remediation demonstrations have been completed using semi-passive designs. Shaw recently completed a USACE-funded field demonstration in Area 11 at the former Whittaker-Bermite site in Santa Clarita, CA (Hatzinger and Lippincott, 2009). After site assessment in Area 11 and development of a localized fate and transport model, a pair of extraction wells was installed approximately 20 meters (66 feet) apart and perpendicular to groundwater flow, and a single injection well was placed between the two extraction wells. A network of 15 monitoring wells screened at various depths in the aquifer was used to assess system performance. Citric acid was added as the electron donor in five active treatment phases. During these phases (1-3 weeks each), the extraction wells were operated at 1.5 to 5.6 gallons-per-minute (gpm) each and citric acid was added in large pulses three times per day, generally followed by the application of chlorine dioxide to prevent well fouling. The system was shut down between the active events (passive mode).

During the 7-month demonstration period, perchlorate concentrations in five of the seven treatment zone monitoring wells declined from ~ 300 μg/L to < 2.5 μg/L, and those in the remaining two treatment zone wells with initial concentrations of ~ 300 μg/L, declined to 16 and 69 μg/L, respectively. Nitrate-N concentrations in five of the seven treatment zone wells declined from ~ 13 - 20 mg/L to < 0.5 mg/L, and the concentration in the remaining two wells declined to < 2.0 mg/L. Perchlorate and nitrate were also declining in one of the three downgradient monitoring wells at the conclusion of the demonstration, suggesting that treated water had reached this well. There were no significant changes in perchlorate or nitrate concentrations in the wells that were outside of the zone of influence of the treatment system.

Dissolved iron and manganese concentrations increased in some of the treatment zone monitoring wells. A slight increase in dissolved arsenic above the PQL of 12 µg/L was also observed in a few wells, but concentrations remained < 50 µg/L in all wells, and there was no elevation in any of the three metals (iron, manganese, or arsenic) in the downgradient monitoring wells. Significant biofouling was not observed during the course of the demonstration, primarily due to the semi-passive groundwater treatment regimen, and the application of chlorine dioxide as a biocide in the injection well. The choice of citric acid as an electron donor also may have reduced the potential for well fouling.

In summary, the results from the pilot test at the Whittaker-Bermite location revealed that *in situ* treatment employing intermittent groundwater pumping and electron donor addition (i.e., semi-passive treatment) could be used to effectively mix electron donor into groundwater, even at a site with complex geology, and that perchlorate concentrations of < 2.5 µg/L can be achieved using this approach. Moreover, the use of an active-passive treatment regimen combined with aggressive biocide application can minimize well biofouling and the associated O&M issues that accompany this common problem with *in situ* groundwater treatment.

Another *in situ* project employing soluble electron donor addition was conducted in a perchlorate-contaminated aquifer at the Longhorn Army Ammunition Plant (LHAAP) in Karnack, TX (Krug and Cox, 2009). At the LHAAP site, a semi-passive barrier was constructed downgradient of a former landfill, where perchlorate was leaching into shallow groundwater at concentrations as high as 2 mg/L. A series of 5 wells were installed on 35 ft centers in a line perpendicular to groundwater flow, with the first, third and fifth serving as extraction wells and the second and fourth as injection wells. During the first active phase of treatment, ~ 3,000 lbs of 60% sodium lactate solution was added to the injection wells over a period of 3 weeks, with the extraction wells operating between 1 and 1.7 gpm. The system was then shut down for 7.5 months after the initial carbon injection. Two additional active phases (injection cycles) were conducted during the 27 month project. Significant reductions in perchlorate were achieved downgradient of the barrier during this demonstration, with 10 of 14 monitoring wells having concentrations < 4 ug/L after the third addition of electron donor, and the 4 remaining wells having concentrations between 4 and 10 ug/L. Biofouling was not an issue during this demonstration. Additional details concerning this project can be found in Krug and Cox, 2009.

Although the number of field trials is limited, and implementation of a full-scale semi-passive system has yet to occur, the initial success of *in situ* semi-passive approaches for perchlorate treatment at the Whittaker-Bermite Site and LHAAP provided optimism that this technology will be viable for explosives remediation in Area 157 at Picatinny. This demonstration provided both performance and cost data for using an injection/extraction system with soluble cosubstrate as a treatment technology for the selected test location.

It should be noted that the term “electron donor” is used to describe the injected carbon substrate for the demonstrations of perchlorate treatment, whereas the term “cosubstrate” is used to describe the carbon source for this demonstration. This semantic difference reflects the fact that the organisms that biodegrade perchlorate are known to utilize the substrate as an energy source (electron donor) while using perchlorate as a terminal electron acceptor. This relationship is very clear. The biodegradative mechanisms of explosives, such as RDX, HMX, and TNT, and the role(s) of the carbon substrate in promoting these mechanisms is less well defined, and may reflect processes other than/ in addition to an electron donor-electron acceptor relationship. Therefore, the more general term “cosubstrate” is used to describe the injected carbon substrate in this instance.

2.3 Advantages and Limitations of the Technology

2.3.1 Advantages

The main advantages of utilizing an *in situ* approach for explosives treatment are as follows:

1. appreciably reduced cost and infrastructure compared to traditional pump-and-treat approaches; and
2. complete destruction of explosives rather than transfer to a secondary medium, such as granular activated carbon.

In addition, the use of a semi-passive injection/extraction design to supply cosubstrate to the subsurface is advantageous in several ways:

1. pumping wells increase the capture of contaminated groundwater and provide a wide treatment zone compared to completely passive donor systems;
2. the system provides active mixing of cosubstrate with explosives-contaminated groundwater, allowing general control of redox conditions and efficient distribution of amendments;
3. the design is dynamic and allows changes in operating parameters, including pumping rates, cosubstrate dosing regimen (i.e., pulsed vs. continuous addition), and cosubstrate type; and
4. the application of a semi-passive rather than a constant-pumping design can significantly reduce system O&M costs, including electrical and biofouling control costs.

2.3.2 Limitations

One potential limitation with this and any *in situ* technology in which organic substrate is added to an aquifer is that the donor addition results in zones of groundwater with low oxidation-reduction potential (ORP). This reduction in ORP is necessary to create conditions conducive to treatment of many contaminants, including anoxic biodegradation of explosives. However, there are secondary geochemical impacts as well. A reduction in ORP results in mobilization of metals (e.g., dissolved Fe (II) and Mn (III) from dissolution of Fe and Mn oxides), sulfide production, and other changes in groundwater geochemistry that impact local groundwater quality. These issues generally occur with the addition of high quantities of slow release substrates, such as vegetable oil, molasses, or polylactate ester (e.g., HRC). In this demonstration, cheese whey was metered and thoroughly mixed with the contaminated groundwater. Mobilization of Fe and Mn, sulfate reduction, and methanogenesis were evident in the monitoring wells near the system's injection well.

A second potential concern with this technology is that microbial fouling may have a significant impact on performance and long-term operational cost. Biofouling is one of the most significant operational issues affecting many *in situ* bioremediation applications. As part of the aforementioned Whittaker-Bermite demonstration for perchlorate remediation, Shaw used chlorine dioxide as an anti-biofouling agent (Hatzinger and Lippincott, 2009). This material was applied daily to wells using an automated system manufactured by Bio-Cide International (the OLAS system using stabilized chlorine dioxide "Oxine" solution). The Bio-Cide system produces chlorine dioxide as a stabilized solution by mixing aqueous sodium chlorite with small amounts of citric acid. This system was chosen over other commercial and developmental units after comparing the hazards associated with each system, and the cost and availability of small commercial units.

Although chlorine dioxide appreciably slowed the onset of biofouling during the Whittaker-Bermite demonstration, it did not completely prevent this phenomenon. Moreover, because the liquid chlorine dioxide is an "oxidizing" anti-fouling agent, it creates oxic conditions in the treatment wells, which likely causes precipitation of dissolved Fe, and subsequent chemical fouling of the well screens. The geochemical conditions at Area 157 at Picatinny Arsenal were less conducive to biofouling than at the Whittaker-Bermite site, due to the lower concentrations of oxygen and absence of nitrate and perchlorate. Therefore, we expected the biofouling issues to be less significant at Picatinny than observed at Whittaker-Bermite.

However, in order to mitigate any potential fouling, we (1) designed the demonstration with intermittent rather than continuous groundwater pumping and co-substrate injection; (2) injected groundwater through a pressurized packer to promote movement of water into the formation; and (3) purchased Tetrakis(hydroxymethyl) phosphonium sulfate (THPS, a readily biodegradable anti-fouling agent) for application in the injection

well if pressure increases were observed during active cosubstrate addition. Fortunately, due to the semi-passive operation, well fouling was not an issue during this demonstration. Injection well pressures during cheese whey addition did not increase to a point where intervention was necessary.

3.0. PERFORMANCE OBJECTIVES

Performance objectives were established for this demonstration to provide a basis for evaluation the performance and costs of *in situ* bioremediation of energetic compounds in groundwater. The primary performance objectives for this demonstration are summarized in **Table 3.1.**

Table 3.1. Performance Objectives.

	Type of Performance Objective	Primary Performance Criteria	Success Criteria	Results: Criteria Met?
1	Quantitative	Reduction of TNT, RDX, and HMX in groundwater	TNT and RDX in groundwater to ≤ 2 μg/L (EPA drinking water Lifetime HA values[1]). HMX in groundwater to ≤ 400 μg/L (EPA drinking water Lifetime HA values).	Yes: All wells in treatment area impacted by cheese whey reached < 2 μg/L for TNT and RDX. HMX was reduced to ≤ 1 μg/L in 5/6 treatment wells impacted by cheese whey.
2	Quantitative	No significant long-term accumulation of common explosives degradation products	2,4-DNT and 2,6-DNT to < 5 μg/L (EPA 10^{-4} Cancer Risk[1]). MNX, TNX, DNX, 2-ADNT, 4-ADNT, 2,6-DANT, 2,4-DANT to < 2 μg/L (no EPA Values available[2])	Yes: 2,4-DNT and 2,6-DNT to < 5 μg/L throughout demonstration in treatment wells. Other intermediates generally < 2 μg/L in all treatment wells.
3	Quantitative	Adequate distribution of cosubstrate within plot	TOC levels > 10 mg/L in local monitoring wells	Yes - TOC levels > 10 mg/L in local monitoring wells receiving cheese whey
4	Qualitative	Biofouling control in injection well	Operation for at least 6 months without well redevelopment.	Yes – No biofouling control necessary. No well redevelopment necessary.

[1] From USEPA (2004). The lowest EPA health advisory values were chosen for each compound.
[2] No EPA health advisory values are available for these compounds.

As summarized in **Table 3.1**, the established performance objectives were each achieved during the demonstration. The following subsections provide details for each of the above performance objectives, including what data were collected and to what extent the success criteria were met.

3.1 Reduction of TNT, RDX, and HMX in Groundwater

The key performance objective of this demonstration was to reduce explosives in groundwater at Picatinny to concentrations below regulatory concern. For TNT and RDX, the EPA has issued Lifetime Health Advisory Limits (MCGL Values) of 2 μg/L, and the equivalent value for HMX is 400 μg/L (US EPA, 2004). Presumably, Federal MCL values for these contaminants, if such are established, will be in this range. New Jersey also has established Interim Ground Water Quality Criteria for both TNT (1 μg/L) and RDX (0.3 μg/L) as previously discussed in Section 1.3. The key performance objective for this demonstration was achieved. Concentrations of TNT in the treatment zone monitoring wells (TZMWs) declined rapidly after the initial cheese whey addition. TNT concentrations were below analytical detection limits (PQL = 0.25 μg/L) in all of the TZMWs by Day 62 of the study, and remained at or below this concentration in all TZMWs except 157MW-6s throughout the remainder of the 565-day demonstration.

The TZMWs had RDX concentrations raging from 5 μg/L to 170 μg/L during the final baseline sampling event (Day -27), with a mean value of 66 μg/L. RDX biodegradation occurred somewhat more slowly than for TNT, but 148 days after the initial injection of cheese whey, RDX concentrations were $\leq$ 5 μg/L in all 6 of the TZMWs, and concentrations in 5 of these wells were < 1.5 μg/L. From Day 222 to Day 565, the concentration of RDX in all of the downgradient TZMWs (157MW-4, 157MW-5, 157MW-7S, 157MW-7D) remained < 1 μg/L, and all were < 0.2 μg/L on Day 565. Thus, more than one year after the final injection of cheese whey on Day 181, RDX was < 1 μg/L throughout the downgradient region of the treatment plot. Upgradient TZMWs 157MW-6S and 157MW-6D also reached < 1 μg/L on Day 148. However, as detailed in Section 5.6.2, this well pair was not impacted by cheese whey after the initial two injections on Day 0 and Day 41, presumably due to an increased rate of groundwater flow and/or slight shift in groundwater flow direction in the plot area. As the TOC from cheese whey declined in these wells during the study, RDX rebounded in both wells, as expected. In those wells where TOC from cheese whey remained above ~ 5 mg/L throughout the study, rebound was not observed. The data show that cheese whey effectively promoted RDX biodegradation throughout the downgradient treatment zone to concentrations less than Federal MCGL values and New Jersey interim action levels, and that as long as a minimal concentration of TOC is maintained, rebound is unlikely.

The HMX concentration in the TZMWs wells ranged from 3.5 to 130 μg/L (mean value 50 μg/L) during the final baseline sampling event. Thus, all wells had baseline concentrations below the EPA MCGL of 400 μg/L. However, a significant decline in HMX was observed in all wells, and by Day 274, each of the 4 downgradient TZMWs

had HMX concentrations < 0.4 μg/L. A slight rebound was observed in Well 157MW-5 at Day 565 (384 days after the last cheese whey injection) but HMX remained < 1 μg/L in each of the other wells throughout the remainder of the study. HMX in upgradient TZMW 157MW-6S rebounded quickly as the TOC concentration in this well declined to < 5 mg/L on Day 222. The HMX concentration in upgradient TZMW 157MW-6D, which reached 0.52 μg/L on Day 148, also increased somewhat. However, as with RDX and TNT, the data from the downgradient TZMWs clearly shown that the addition of cheese whey to the Picatinny aquifer effectively promoted HMX biodegradation to sub μg/L concentrations. Moreover, as long as TOC concentrations were maintained > 5 μg/L, rebound of HMX was not observed.

A number of other nitroaromatic compounds also were quantified via EPA 8330 analysis throughout the demonstration, including several nitrobenzenes and nitrotoluenes, 2,4,6-trinitrophenol (picric acid), 2,4,6-trinitrophenylmethylnitramine (Tetryl), and pentaerythritol tetranitrate (PETN). Among these compounds, 1,3,5-trinitrobenzene (1,3,5-TNB) was present throughout the demonstration plot at ~ 10 to 70 μg/L prior to cheese whey injection. A rapid decline in the concentrations of this compound was observed in all TZMWs (< 0.25 μg/L by Day 62) and the concentration remained < 0.6 μg/L in all TZMWs until the final samples for this compound were collected on Day 420. Among the other compounds detected in the treatment plot, 2,4-dinotrotoluene (2,4-DNT) and 2,6-dinotrotoluene (2,6-DNT) also were biologically degraded in the treatment zone wells. 2,4-DNT was detected consistently in wells 157MW-3, 157MW-5, 157MW-6D, 157MW-6S, 157MW-7D, and 157MW-8D during baseline sampling at concentrations ranging from ~ 0.5 to 1.7 μg/ L (0.25 μg/L PQL). The compound was not detected in any of the other wells, except the extraction wells during system operation. After cheese whey addition, 2,4-DNT declined to <0.25 μg/L in the TZMWs by Day 33, and with a few exceptions, remained below this concentration throughout the demonstration. There was no apparent decline in 2,4-DNT in CZMWs 157MW-3 or 157MW-8D during the study. Similar results were observed for 2,6-DNT in the same wells.

3.2 No Long-Term Accumulation of Degradation Intermediates

Another critical performance objective for this demonstration was to show that there was no long-term accumulation of common daughter products of TNT and RDX biodegradation under anoxic conditions. This performance objective also was met during the study. Two common TNT daughter products, 4-amino-4,6-dinitrotoluene (4-ADNT) and 2-amino-2,6-dinitrotoluene (2-ADNT) were present from ~ 1 to 120 μg/L in groundwater monitoring wells at the demonstration site during baseline sampling. These products are formed from an initial reduction of one nitro-group on TNT to an amino group, and may either have been present in the water released from the facility during processing, or have formed after disposal to land surface via biological reactions. A rapid reduction in the concentrations of both of these compounds in groundwater was observed following injection of cheese whey. In fact, neither TNT daughter product was present

above the analytical PQL of 0.25 μg/L in the TZMWs by Day 148. There was a slight rebound of these compounds in upgradient wells 157MW-6S and 157MW-6D after this time, but each of these wells was not impacted by cheese whey after the initial injection, as previously discussed. For each of the other TZMW wells, concentrations of these compounds remained below detection (< 0.25 μg/L) from Day 148 to Day 420. There was no appreciable increase or decrease in the concentration of these compounds in the wells outside of the treatment zone.

With the exception of one detection in well 157MW-5, 2,4-diamino-6-nitrotoluene (2,4-DANT) and 2,6-diamino-4-nitrotoluene (2,4-DANT) were not present in Picatinny groundwater prior to whey injection. These compounds, each of which is an expected degradation intermediate of TNT, increased in the TZMWs as TNT biodegraded and then declined in concentration to below their respective PQL values by Day 98 and for the duration of the demonstration in TZMWs 157MW-4, 157MW-5 157MW-7S and 157MW-7D**.** The compounds declined and then rebounded in Well 167MW-6S once all the TOC from cheese whey was depleted.

The concentrations of the common RDX daughter products MNX, DNX, and TNX increased in one or more of the TZMWs, but not in the CZMWs. However, the total concentrations were < 20 μg/L in all cases, and generally much lower, and all three nitroso-derivatives were transient. The production of these intermediates is expected during reductive biodegradation of the nitramine, and clearly indicates that the explosive is being biologically reduced in the treatment area wells. A significant decrease in the concentrations of each of these daughter products was observed during the demonstration, and all were near or below detection by Day 420 of groundwater monitoring. All three products remained below detection in wells sampled on Day 565. Overall, the data suggest that each of the RDX nitroso-derivatives were further biodegraded in the aquifer.

3.3 Adequate Distribution of Cosubstrate

Total organic carbon (TOC) was utilized as a measure of cheese whey (cosubstrate) distribution within the aquifer underlying the demonstration plot. A significant increase in TOC concentration within the treatment zone was observed following the initial system operation and injection of cheese whey. TOC in all wells in all TZMWs quickly reached concentrations exceeding 90 mg/L after the initial injection, with some wells exceeding 200 mg/L. The initial goal was to achieve at least 10 mg/L TOC in each well. TOC in monitoring wells outside of the treatment zone did not increase above the background concentration. Significant increases in TOC were again observed after the third and fourth injection events in all wells except 157-MW6S and 167 MW-6D. These wells were upgradient of the injection well, and it is presumed that they were not impacted by the later whey additions due to an increased rate of groundwater flow in the area. The gradient in the treatment area was relatively flat and prone to slight alterations with the water table as discussed in Section 5.2.2.2. However, the intermittent pumping

design was extremely effective at distributing cosubstrate within the core treatment zone as indicated by TOC concentrations in downgradient wells.

3.4 Biofouling Control in Injection Well

Microbial biofouling is a significant concern with any *in situ* remedial system, and particularly with those requiring active pumping. During this demonstration, techniques to control biofouling included: (1) pumping groundwater intermittently rather than continuously, and reducing the active pumping phase as much as possible; (2) injecting large quantities of cosubstrate during the pumping phase; and (3) injecting groundwater through a pressurized packer to promote movement of water into the formation. In addition, the injection well was designed with a downhole pump connected to a recirculation loop so that the anti-fouling amendment Tetrakis(hydroxymethyl) phosphonium sulfate (THPS) could be added and distributed within the well if necessary based on pressure in the injection well. During the demonstration, addition of THPS was not necessary because the first three strategies were effective at controlling well fouling. Significant pressure increases were not observed in the IW during the four pumping phases, so additional control or well rehabilitation measures were not necessary. Most importantly, using the pumping design primarily as a means to mix cosubstrate into the aquifer was determined to significantly reduce the potential for biofouling and the associated costs with this issue.

4.0 SITE DESCRIPTION

4.1 Selecting Test Site(s)

The semi-passive recirculation cell design used for this ESTCP project is expected to be widely applicable at DoD sites for mixing cosubstrate and other amendments in explosives-contaminated groundwater. The chosen demonstration site at Picatinny has characteristics to facilitate a timely, cost-effective, and clear evaluation of the proposed technology. Site conditions are also reasonably "typical" (relative to other DoD sites with energetic compound contamination) such that application of the proposed technology can be readily transferred. Specific criteria used in site selection included the following:

- *High horizontal hydraulic conductivities (i.e., sandy aquifer).* Low hydraulic conductivity soil would limit mixing of amendments and dissolved contaminants, thereby limiting the effectiveness of the proposed technology in the one-year time frame;

- *Depth to contaminated aquifer < 100 ft.* Relatively shallow depths will limit costs associated with well installation and operation;

- *RDX groundwater concentration greater than 50 μg/L in demonstration area.* Elevated RDX concentrations will facilitate evaluation of technology effectiveness with respect to RDX treatment;

- *Co-contaminants not present at high levels.* High co-contaminant concentrations could be toxic to microorganisms that are able to biodegrade energetic compounds;

- *Good availability and quality of existing site data*. A well-characterized site will be selected to reduce overall project cost and risk.

Picatinny was selected as the location for this demonstration during the proposal phase, as the project is a collaborative effort between Shaw and the ETD at Picatinny. After a review of existing data and discussions with on-site personnel, two locations (Group I Area; Site 40 & Site 157, respectively) were chosen as possible demonstration sites. Additional details concerning the Group I Area sites are provided in Section 4.2. Based upon field investigations undertaken from 1996 to 2002, each of the two test locations is characterized by shallow groundwater (< 35 ft bgs) contamination with RDX, HMX, TNT, 2,4-DNT, and 2,6-DNT. The occurrence and level of these compounds varies considerably among the monitoring wells installed at each location. However, concentrations of RDX $\geq$ 150 μg/L and TNT $\geq$ 47 μg/L were observed in both areas during an August 2002 sampling event (the most recent data available prior to the ESTCP site investigation work). The explosive types and concentrations appear to be representative of those present in groundwater underlying production areas (e.g., Davis et

al., 2004) and training ranges such as Camp Edwards, Mass. (Clausen et al., 2004) where this technology could be applied in the future. In addition, although levels of common alternate electron acceptors, including nitrate and sulfate, are reasonably low, the groundwater chemistry at the Group I Area is not atypical of that in the Northeast United States. Moreover, the site does not contain any unusual co-contaminants. Thus, the data from either location (Site 40 or Site 157) should translate to other facilities with explosives in groundwater.

An initial characterization of the Group 1 Area, including Sites 40 and 157 was performed to support a remedial-investigation/feasibility-study (RI/FS) of remedial options in this area (Gerdes et al., 2004). This evaluation provides data concerning site history, soils and groundwater contamination with explosives, and the local geology, hydrogeology, and groundwater geochemistry. In addition, a bioremediation remedy was included as a possible remedy for groundwater contamination in this area in the FS report. Thus, the two Picatinny locations each meet the basic criteria defined for a demonstration site for this investigation.

The one key difference between the two sites is that Area 40 lies behind an active explosives packing facility (Building 810), whereas Area 157 is in an area with primarily inactive operations. Thus, access to Area 40 requires permission from the Building 810 supervisor, and such access could not be granted during active operations based on Picatinny safety regulations. Conversely, access to Site 157 is generally unlimited. Because the general contaminant and geological conditions at the two locations were similar, but the access restrictions differed significantly, Area 157 was ultimately chosen as the demonstration site. Prior to this selection, however, a full evaluation of site data was performed, including collection of groundwater samples from all monitoring wells in both areas to quantify explosives concentrations at the current time. Additional details concerning both sites are provided in the subsequent sections.

4.2 Test Site History/Characteristics

4.2.1 Picatinny Arsenal

Picatinny is located approximately four miles north of the City of Dover in Rockaway Township, Morris County, New Jersey. State Route 15 skirts the southern end of Picatinny, and Interstate 80 is about one mile southeast of the main entrance **(Figure 4.1)**. The land area consists of 6,491 acres situated in an elongated classic U-shaped glacial valley that trends northeast-southwest between Green Pond Mountain and Copperas Mountain on the northwest and an unnamed hill on the southeast (Sims, 1958). Most of the buildings and other facilities at Picatinny are located on the narrow valley floor or on the slopes along the southeast side. Several firing and testing ranges are located on Green Pond Mountain.

In general, the areas that surround the arsenal are suburban and summer vacation areas because of the numerous small lakes and many mountains. Some of the nearby populous

areas are Morristown, Morris Plains, Parsippany, Troy Hills, Randolph Township, and Sparta Township. Picatinny is owned and operated by the U.S. Army, and was a major source of munitions for World War I (WWI), World War II (WWII), the Korean War, and the Vietnam Conflict. During those periods, Picatinny was involved in the production of explosives, rocket and munitions, propellants, pyrotechnic signals and flares, fuses, and metal components. Currently, the primary mission of Picatinny is research, development, and engineering of munitions and weapons.

4.2.2 Demonstration Area – Group 1 Sites

The demonstration will be performed at Site 157. This site is defined as one of four locations within the Group 1 Area west of Picatinny Lake in the central portion of the Arsenal **(Figure 4.2)**. The Group 1 study sites, which were defined in a recent RI/FS document prepared for this area (Gerdes et al., 2004) consist of the following:

Site 40:	Buildings 809 and 810, Explosives Manufacturing Wastewater Treatment Plant (WWTP) [Defense Site Environmental Restoration Tracking System (DSERTS) #079];
Site 93:	Buildings 800 and 807, Ordnance Facilities (DSERTS #139);
Site 156:	Buildings 813, 816, and 816-B, Ordnance Facilities (DSERTS #151); and,
Site 157:	Buildings 820, 823, and 824 Ordnance Facilities (DSERTS #152).

The buildings listed above comprise the majority of the 800 Building area. This 2,400-ft line of buildings, known as the melt load line or completed rounds division, was established to load, assemble, and pack for shipment various calibers of loaded shells and bombs. The buildings are interconnected by conveyors and walkways to permit the smooth flow of materials in the production process.

4.2.3 Site 157 – Buildings 820 & 823

Site 157 was selected as the Demonstration Site for this ESTCP Project based on contaminant concentrations, the existence of 5 monitoring wells, availability of site characterization data, and non-restricted site access. Site 157 consists of buildings 820 & 823. Both buildings were used as large-caliber projectile loading plants.

Building 820 was constructed in 1930 as a packing and shipping facility for the completed rounds loading production line. Operations included packaging, palletizing, strapping, and stenciling of ammunition items. Building 820 has currently been reactivated as an ammunition repack and surveillance facility. Ammunition materials are inspected and problem lots pulled for disassembling and repacking. According to interviews with personnel, no energetic wastes are presently stored, disposed of, or generated at Building 820. Repackaging and surveillance operations are generally dry;

therefore, no wash down water is produced. However, spent spray paint cans and lubricating containers are generated at Building 820. These waste materials are stored in an RCRA-approved satellite waste accumulation area.

Building 823 is thought to be the primary source for contamination in Area 157. A photo of the north side of this building is provided as **Figure 4.3**. The building was constructed in 1930 as a melt-load facility responsible for the loading of melted TNT and RDX explosives into shells positioned on a conveyor. Overpour from the operation was collected in a catch trough below the conveyor. Wash down water produced during decontamination activities at Building 823 was collected by troughs, which ran along the building **(Figure 4.4)**. A settling and filtering system was used to treat operation wastewaters and wash down waters. The wastewater and wash down water were discharged to collection boxes located northeast of Building 823 **(Figure 4.5)**. The collection boxes ultimately discharged to Picatinny Lake. Building 823 also had a rotoclone, which was used to filter airborne energetic particles. There is historical evidence of uncontrolled discharge of explosives-contaminated water in and around Building 823. A 1965 investigation cited volumes of wastewater flowing over the surrounding terrain. Investigations conducted in 1974 found excessive condensation of explosives from the melt kettles collecting on the building ceiling. In another report later that year, cracks in the floor were found to contain energetic materials. Since the wastewater filtering system at Building 823 was a 1950s process modification, it is likely that previous wastewater was discharged untreated to Picatinny Lake (Gerdes et al., 2004).

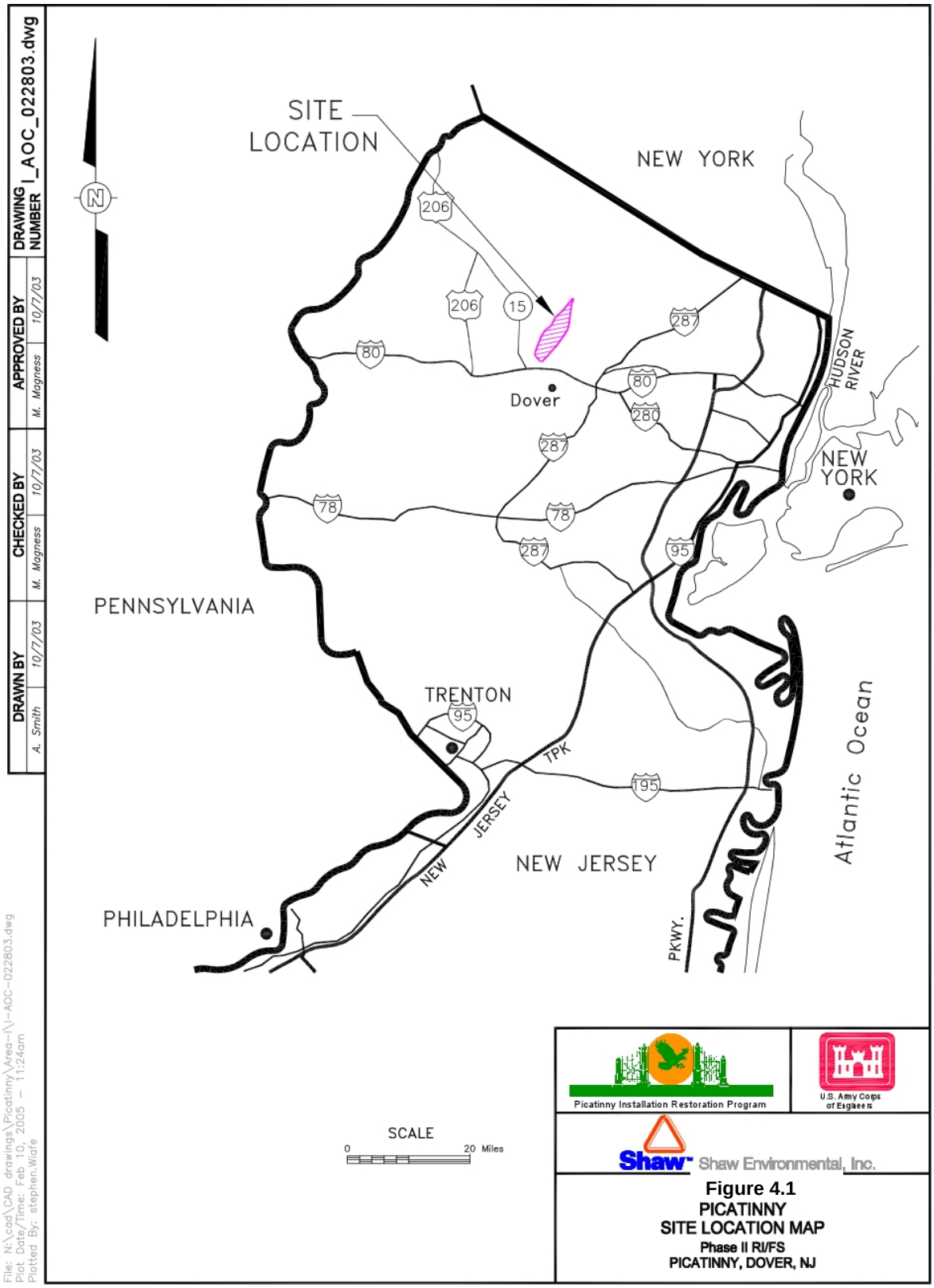

Figure 4.1. Location of Picatinny Arsenal
(from Gerdes et al., 2004).

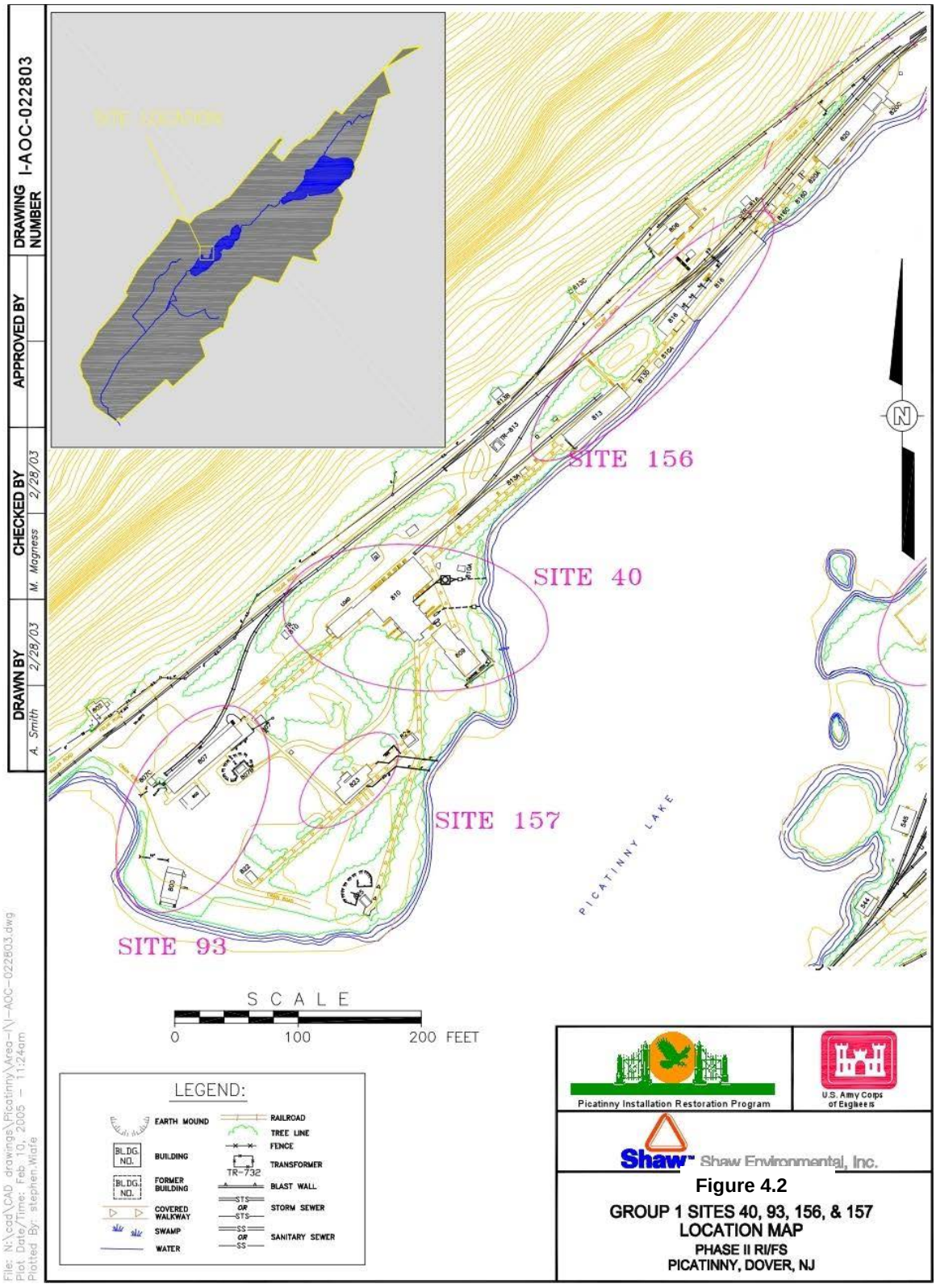

Figure 4.2. Location of Group I sites. The demonstration was conducted at Site 157 (from Gerdes et al., 2004).

Figure 4.3. Southeastern view of Building 823 in Area 157.

Figure 4.4. Troughs used to carry washdown water located on the north side of Building 823 in Area 157.

Figure 4.5. Collection boxes for wastewater and washdown water located northeast of Building 823 in Area 157.

4.2.4 Local Topography and Surface Water Hydrogeology

The Group 1 site is bounded to the northwest by the steep ridges of Green Pond Mountain and to the southeast by the shoreline of Picatinny Lake. Within Group 1, there is very little topographic relief, however, Green Pond Mountain rises abruptly to the northwest to elevations of over 1,000 ft mean sea level (msl). The highest surface elevation within Group 1 occurs adjacent to the steep ridges of Green Pond Mountain along Fidlar Road, at approximately 725 ft msl. The ground surface at Group 1 slopes gently to the southeast with the lowest land elevations occurring on the shoreline of Picatinny Lake at approximately 710 ft msl.

In the main valley of the arsenal, surface water flows overland into the valley floor from the ridges that bound the valley to the northwest and southeast. Surface water then drains along the axis of the valley, from northeast to southwest. Lake Denmark is located in the valley on the northeast side of the installation. Surface water discharges from Lake Denmark to Burnt Meadow Brook, which flows to Green Pond Brook. Green Pond Brook then flows to the southwest and discharges to Picatinny Lake. Picatinny Lake, located in the geographic center of Picatinny, is approximately 5,300 ft long and averages 1,000 ft wide. The lake is a maximum of 20 ft deep yielding a capacity of 165 million gallons. Picatinny Lake discharges southwest of the Group 1 sites into Green Pond Brook, which eventually discharges to the Rockaway River about one mile southeast of Picatinny. From this confluence, the Rockaway River flows east to the Boonton Reservoir, an 8.5-billion gallon water source for Jersey City.

In Group 1, surface water drains primarily overland from Green Pond Mountain, through Group 1, and into Picatinny Lake. The topography and surface water hydrology of this area has been altered by installation activities that include buildings, roadways, former railroads, sanitary sewers, and drainage ditches. In the past, Picatinny Lake has received numerous wastewater discharges, including effluent from the Building 809 explosive WWTP, floor washdown from explosive production, and various spills. Recently, the only wastewater discharge that Picatinny Lake has received is non-contact cooling water from the Building 506 power plant (Site 63/65), located outside of the Group 1 Study Area. This was a permitted discharge to the Lake and is no longer conducted due to the ongoing heat decentralization plan.

4.2.5 Group I Geology

A total of 18 monitoring wells were installed and three soil borings were completed to characterize the geology of the Group 1 study sites prior to the initiation of this ESTCP project. The first monitoring wells were installed in this area in 1996. Of the 18 wells, 5 were installed in Area 157. The construction details of these wells are provided in **Table 4.1.** Four of the wells are installed in unconsolidated glacial sediments (157 MW1- 157 MW-4) and one is a bedrock monitoring well (157MW-1D). It should be noted that 157MW-1D is also shown as 157MW-1B in a few figures. **Figure 4.6** presents the location of the 5 monitoring wells previously installed in Area 157, and includes well 157-MW5, which was installed for this ESTCP project, as described in Section 5.3.1. In addition, **Figure 4.6** includes locations of Hydropunch (HP) and soil sampling (SS) performed during the current project. The Hydropunch and soil sampling activities are discussed in detail in Section 5.2.3.

Table 4.1. Well Construction Details for Area 157 Monitoring Wells.

Well I.D.	Well Diameter (inches)	Screened Interval (ft bgs)	Total Depth (msl)	Land Elev. (msl)	TIC Elev. (msl)	Aquifer
157MW-1	4	24.1-34.1	685.00	718.61	720.96	Unconsolidated
157MW-1D	4	134-144	573.66	717.50	719.60	Bedrock - Hardyston Quartzite
157MW-2	4	25.8-35.8	684.66	716.99	719.90	Unconsolidated
157MW-3	4	26.6-36.6	684.62	717.86	720.57	Unconsolidated
157MW-4	2	24-34	683.3	717.29	719.63	Unconsolidated
157MW-5	2	24.5-34.5	NS	718.30	717.8	Unconsolidated

A geologic cross-section of this area is presented in **Figure 4.7**. Deltaic and sublacustrine sand with varying percentages of silt, clay, and gravels was encountered within the unconsolidated unit at Group 1. This unit is discontinuous across the valley, however it was logged in boreholes advanced along the delta extending into Picatinny Lake where the Group 1 sites are located. This unit extended from the ground surface to 107 ft below ground surface (bgs) in boreholes advanced during the field investigation

and was logged as primarily fine to coarse, sub rounded to rounded sand, which was generally loose and well graded. The secondary component varied across the study area and with depth. At Site 40, the secondary component was generally sub angular to rounded gravel ranging from 10 to 40 percent (%) of the total matrix, and coarsened with depth. At Site 157, the secondary component of silt and clay decreased with depth to little or no fine material. The base of this unit is characterized by 20 to 25 ft of gravel, cobbles and boulders to the top of bedrock. The Hardyston Quartzite was identified at Site 40 and Site 157 during installation of the bedrock monitoring wells (3). The formation was described from cuttings as a medium to fine-grain, green orthoquartzitic sand. The formation unconformably overlies the Precambrian basement rock. The depth to bedrock from ground surface ranges between 86 ft at 40MW-2D to 107 ft at 40MW-1D.

4.2.6 Group I Hydrogeology

Two distinct aquifers, the unconsolidated and bedrock were characterized during the previous field investigations. The unconsolidated aquifer was encountered along the entire western shore of Picatinny Lake and in the small deltas, which extend into the lake, with the exception of Site 156, where competent bedrock was encountered at less than 10 ft bgs. This aquifer is thickest along the shores of the lake adjacent to the delta and pinches out where bedrock is close to the ground surface. The total thickness of this aquifer on the delta ranges between 86 ft at 40MW-2D to 107 ft at 40MW-1D.

The region-wide hydrogeology of Group 1 was investigated by conducting water level measurements at the 18 regional monitoring wells, and performing both falling and rising-head slug tests on 13 of the wells. The slug tests were performed initially on two of the wells in Area 157. Additional slug testing was conducted for this demonstration. A detailed discussion of the Area 157 hydrogeology is discussed in Section 5.2.2 (groundwater elevations and gradients) and Section 5.2.4 (slug testing to estimate hydraulic conductivity in the demonstration area).

4.2.7 Groundwater Contamination

Eighty-one groundwater samples were collected from the Group 1 Sites prior to the beginning of this ESTCP demonstration project, including four rounds of monitoring well sampling, discrete interval sampling during deep monitoring well installation, Hydropunch sampling, and piezometer sampling. The analytical results of key parameters from sampling the 18 groundwater monitoring wells (four rounds), nine piezometers installed along the shoreline of Picatinny Lake, and nine Hydropunch samples are summarized on **Figure 4.8**, and further detail is available in Gerdes et al., 2004. In general, the RDX groundwater contamination is more widespread than the TNT groundwater contamination. TNT was detected above its LOC of 2 μg/L in 18 groundwater samples, collected from seven monitoring wells. Concentrations of TNT, above the LOC, ranged from 2.48 μg/L to 400 μg/L. The maximum detected TNT concentration occurred in 40MW-1 in January 1999. The TNT concentration in 40MW-1 fluctuated between 38.9 μg/L to 400 μg/L over four sampling events. The TNT

concentration detected in 40MW-1 was 82.0 μg/L, in August 2002. RDX was detected above its LOC of 0.61 μg/L in 46 groundwater samples, collected from monitoring wells, Hydropunch points, and discrete interval samples collected during deep monitoring well installation. Concentrations of RDX, above the LOC, ranged from 0.70 μg/L to 490 μg/L.

The maximum detected RDX concentration occurred in 40MW-2, in January 1999. The concentration of RDX in 40MW-2 fluctuated between 5.81 μg/L and 490 μg/L over the four sampling events. The most recent detected concentration of RDX in 40MW-2 was 80.0 μg/L in August 2002. The RDX and TNT plumes are delineated to the north and west by Hydropunch samples 40HP-5 and 40HP-6, and monitoring wells 40MW-4, 93MW-1, 93MW-2, and 93MW-3. RDX was detected in samples collected from 93MW-1 in October 1996 and January 1999 at concentrations of 2.63 μg/L and 2.30 μg/L, respectively. However, RDX was not detected in 93MW-1 during the August 2002 groundwater sampling event. The plumes are delineated to the south and east by the shallow piezometer and surface water samples collected along the shoreline of Picatinny Lake. RDX has been detected above its LOC in deep monitoring well samples 40MW-1D and 157MW-1D at relatively low levels (1.8 μg/L and 0.7 μg/L, respectively in August 2002). From the discrete interval sampling conducted during the installation of the deep monitoring wells, it is evident that the RDX plume is primarily located in the unconsolidated aquifer.

Based on the analytical results from groundwater samples collected in August 2002, preliminary plume maps of the RDX and TNT contamination were developed. These plume maps were augmented with the results from the site investigation work in 2004 and 2005 for this ESTCP project, which includes Hydropunch data and groundwater monitoring data from newly installed wells. The updated plume maps are presented in Section 3.5.4. A discussion of the groundwater flow direction and velocity is provided in Section 3.5.3.2.

4.2.8 Groundwater Geochemistry

The historical geochemical data for the Group 1 Sites are provided in Gerdes et al., 2004. Redox potentials recorded during the August 2002 sampling of Group 1 groundwater monitoring wells ranged from -108.1 mV to 342.1 mV, and were predominantly within the range of mildly reducing conditions. Fe(II) concentrations analyzed in August 2002, using the HACH Method 8146, ranged from 0.00 mg/L to 0.09 mg/L. Sulfate concentrations ranged from 4 to 22 mg/L. Redox potentials recorded during the March 2003 natural attenuation assessment ranged from -230.2 mV to 41.4 mV, and were predominantly within the range of mildly to strongly reducing conditions. Groundwater pH values in Area 157 overburden wells ranged from 4.8 to 6.3. Area 157 groundwater geochemical parameters measured during pre-demonstration site assessment are presented in Section 5.2.

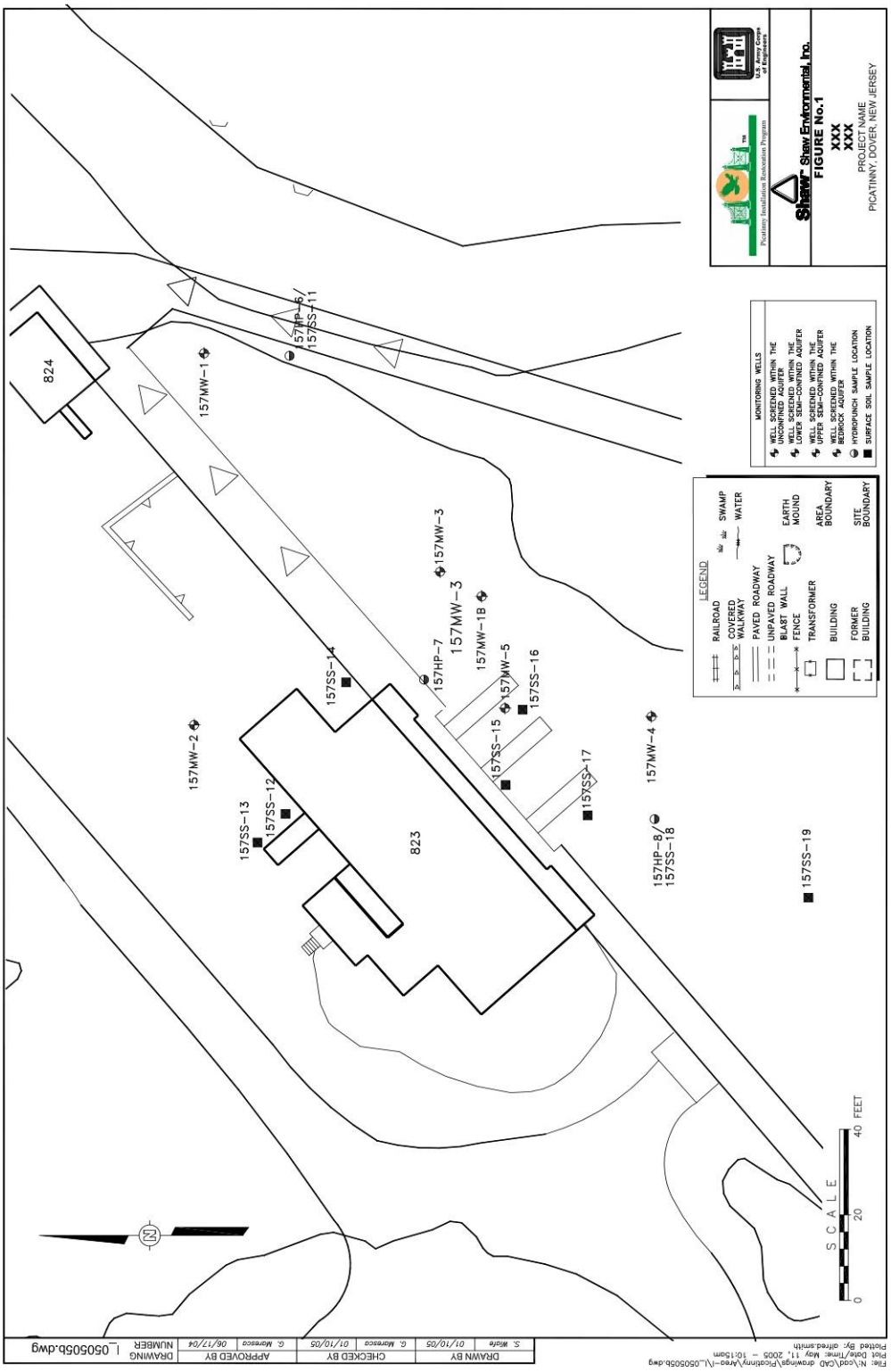

Figure 4.6. Location of the monitoring wells (MW), hydropunch samples (HP) and soil samples (SS) in Area 157. Wells 157MW-1 to 157MW-4 were installed during previous investigative work.

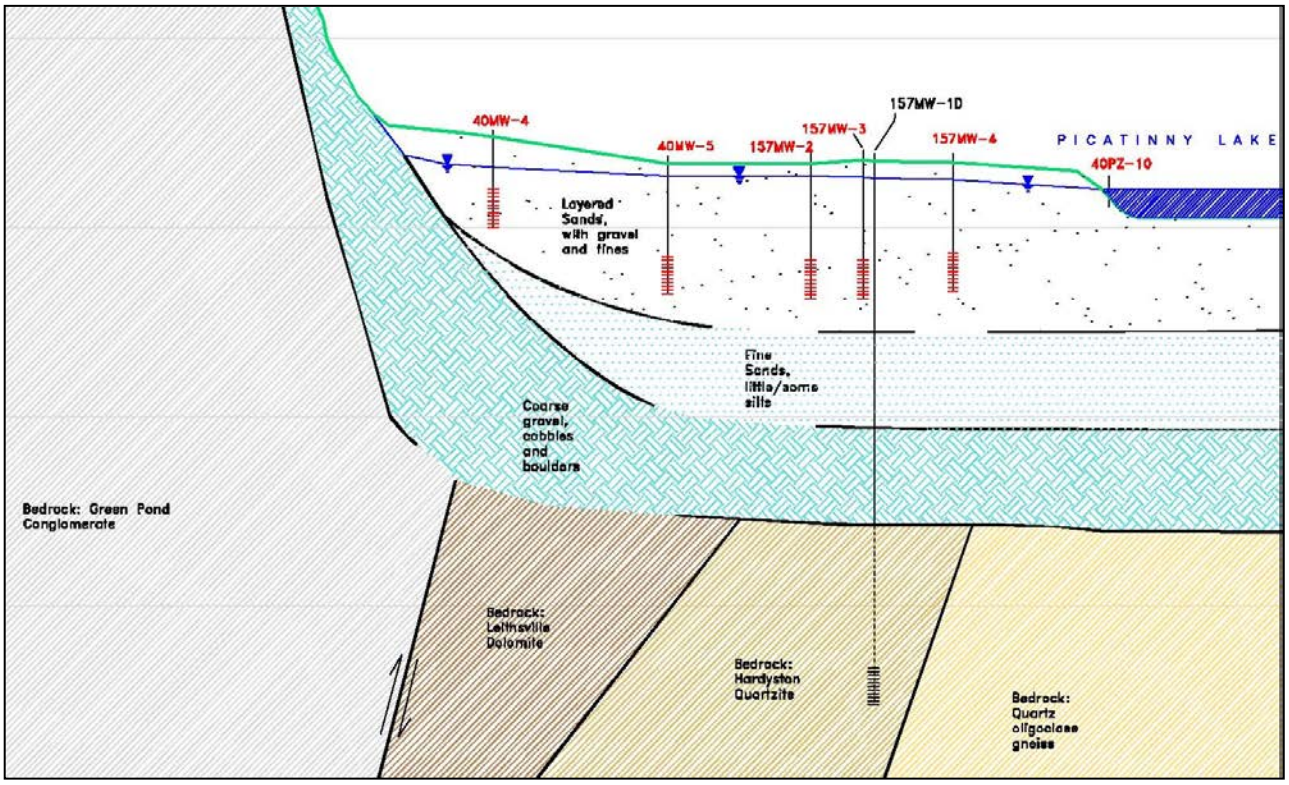

Figure 4.7. Geology of Group I Sites: Area 157 and Area 40
(modified from Gerdes et al., 2004).

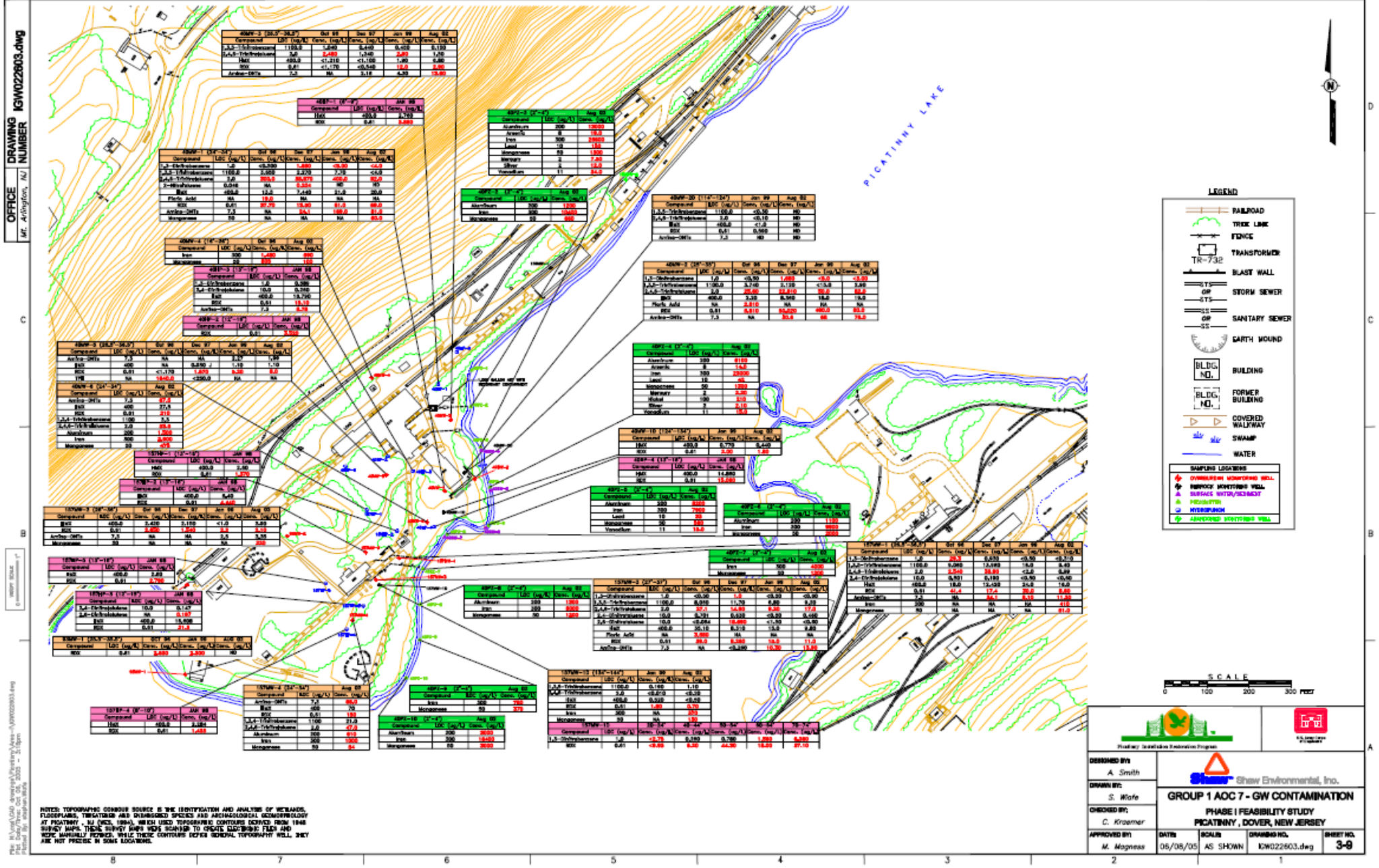

Figure 4.8. Explosives concentrations in groundwater samples collected from Site 157 between April, 1996 and August, 2002 (from Gerdes et. al, 2004).

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4.2.9 Surface, Subsurface, and Sediment Contamination

Surface soil samples were collected at Site 157 during the Phase II RI as described in detail in Gerdes et al., 2004 (see **Figure 4.9**). RDX was detected above its LOC of 26 mg/kg at three locations. The RDX exceedences were reported in samples 157MW–1A (3,100 mg/kg), 157SB-1A (36.0 mg/kg) and 157SS-3C (9,600 mg/kg). Samples 157MW-1A and 157SS-3C were collected approximately 20 ft apart along the wastewater discharge line from Building 823 to Picatinny Lake. Sample 157SS-3C also contained the highest levels of TNT (110 mg/kg), picric acid (15 mg/kg), HMX (2,200 mg/kg) and nitrocellulose (1,400 mg/kg). The TNT and picric acid concentrations in 157SS-3C exceeded their LOCs of 51 mg/kg and 2.3 mg/kg, respectively. PETN concentrations in sample 157MW-1A (350 mg/kg) and sample 157SB-1A (57.0 mg/kg) exceeded its LOC of 22.8 mg/kg. There was no LOC established for nitrocellulose. HMX was not detected above its LOC of 10,000 mg/kg. No metals or anions were reported at concentrations above LOCs.

Additional surface soil samples, 157SS-5 through 157SS-10, were collected based upon these results. Samples were collected in the vicinity of the two walkways and drainage troughs near sample location 157SS-3 and along the former wastewater discharge lines in areas where there were no previous samples collected. RDX was only detected above its LOC in sample 157SS-7, at a concentration of 270 mg/kg. No other explosives were detected above LOCs in any of the additional samples collected for lateral delineation of this AOC. Collection of additional soil surface samples as part of the pre-demonstration activities to identify potential source areas in Area 157 is discussed in Section 5.2.3.

A total of 47 subsurface soil samples were collected to address Area 157 contamination concerns between 1996 and 2002. Sample 157SS-3D, collected from 2-4 ft bgs and analyzed on-site, had a reported RDX concentration of 460 mg/kg. This concentration decreased from the surface soil level of 9,600 mg/kg, but still exceeded the LOC for RDX (26 mg/kg) (**Figure 4.9**).

Analyses performed on subsurface soil samples collected from boreholes advanced at Site 157 indicate subsurface soil explosive contamination near monitoring well 157MW-1. This well was installed on the northeast side of Building 823 near the below-ground settling tank. RDX and HMX were detected to 25 ft bgs, while TNT was detected at both the 5-7 ft bgs interval and the 15-17 ft bgs interval. RDX concentrations exceeded the LOC of 26 mg/kg at the 10-12 ft bgs interval (68 mg/kg).

Three sediment and surface water samples were collected at Site 157 along Picatinny Lake during the Phase II RI. Sample 157SW/SD-1 was collected from the shoreline east of Building 820. Lead and mercury were detected above the sediment LOCs of 38.8 mg/kg and 0.249 mg/k in sample 157SD-1, at concentrations of 44.1 and 1.30 mg/kg, respectively. Neither lead nor mercury was detected in the corresponding surface water sample. Samples 157SW/SD-2 and

157SW/SD-3 were collected at Building 823 where two aboveground explosives drainage troughs discharge to the lake. Surface water sample, 157SW-2, contained 6.79 μg/L of RDX, above the LOC of 0.61 μg/L. This sample was collected at the outfall for explosives wash down discharge trough. Surface water sample 157SW-3, collected at the outfall for the discharge line associated with the below-ground settling tank, contained 2.12 μg/L of RDX. The associated sediment samples did not contain any detectable explosives. No VOCs, SVOCs, or metals were detected in surface water samples 157SW-2 and 157SW-3.

Sediment and surface water sample 53SD/SW-23 was collected from Picatinny Lake approximately 100 ft southeast of sample 157SD/SW-3. This sample did not contain any explosives in either the surface water or sediment. On-site analysis of the sediment samples indicated levels of the following pesticides were in excess of their LOCs in sample 157SD-2: beta-BHC (0.088 mg/kg), delta-BHC (0.050 mg/kg) and heptachlor (0.038 mg/kg).

Additional sediment samples were collected Site 157 to provide further information on the nature and extent of explosives and metals contamination within the lake. Two samples, 157SD-4 and 157SD-5, were collected approximately 10 ft from shore near sample location 157SD-2, and analyzed for explosive, metals and SVOCs. Results for sample 157SD-4 exceeded LOCs for naphthalene (LOC = 0.03275 mg/kg) at a concentration of 0.0690 mg/kg, mercury (LOC = 0.249 mg/kg) at a concentration of 0.440 mg/kg, and silver (LOC = 1 mg/kg) at a concentration of 1.50 mg/kg. Explosives were not detected in samples 157SD-4 and 157 SD-5.

4.3 Present Operations

There were no ongoing remedial operations in Area 157 or in any of the other three regions composing the Group I Sites during this project.

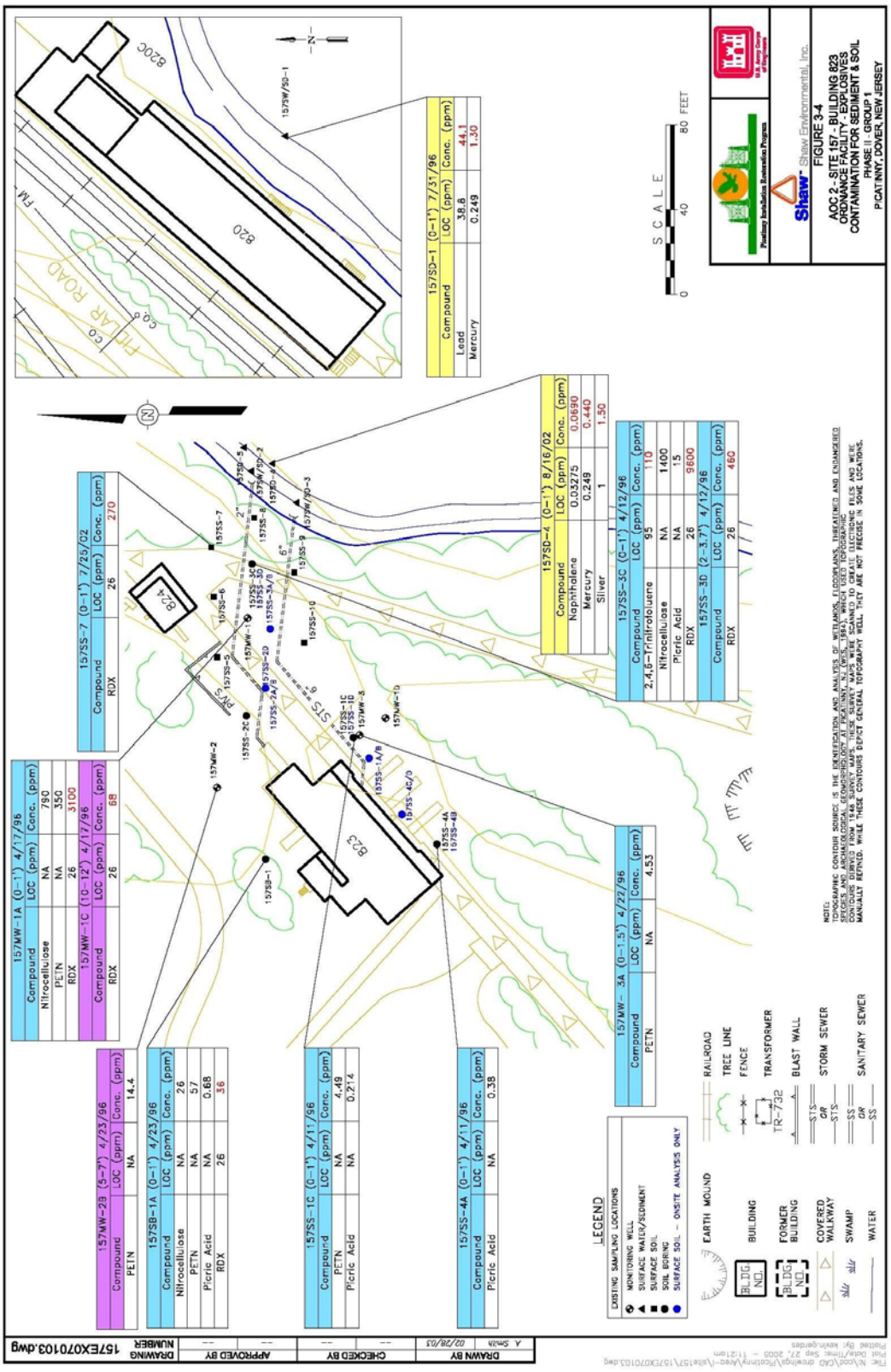


Figure 4.9. Explosives concentrations in surface soil samples collected from Site 157 between April, 1996 and August, 2002 (from Gerdes et. al, 2004).

5.0 TEST DESIGN

Design of the *in situ* mixing and amendment injection system required detailed site-specific knowledge of the contaminant distribution, hydrogeology and microbiology. Specific system parameters directly influenced by the hydrogeology and microbiology include amendment (nutrients and cosubstrate) selection, spacing of the injection/extraction and monitoring wells, pumping rates and schedules, well screen intervals and depths, and amendment injection rates. All available site characterization data was reviewed prior to selecting the location of the demonstration (see previous summary in Section 4). However, additional local characterization of the selected demonstration location (Area 157) was required to facilitate system design. Therefore, the activities described within this section were conducted in order to attain the needed site-specific information required for final system design. Specific activities included laboratory microcosms and column experiments to evaluate biodegradation kinetics, monitoring well installation, groundwater sampling to determine contaminant distribution and hydraulic gradients, supplemental soil and groundwater investigation to identify potential contaminant sources and delineate the dissolved contaminant plume, and slug and pump testing to determine aquifer hydrogeologic parameters.

The results from the treatability studies and site characterization work were used to design the test system and to determine the most effective means to operate this system. As detailed previously, a groundwater recirculation design was used to distribute and mix cosubstrate with explosives-contaminated groundwater and to deliver that substrate to indigenous bacteria **(Figure 2.1** and **Figure 2.2)**. The recirculation system consisted of two groundwater extraction wells and one groundwater injection well installed in the aquifer cross-gradient to groundwater flow. The groundwater was removed from the aquifer through the two extraction wells, amended with cheese whey as a cosubstrate at the surface, and then recharged into the formation through the single injection well. A "semi-passive" (also called "active-passive") mode of operation was utilized to mix cosubstrate with groundwater (active phase) and then to allow degradation to occur under static conditions (passive). This type of operation, as previously detailed, is optimal to promote contaminant degradation while limiting injection well biofouling and other O&M issues. Baseline sampling, treatment phase sampling during 4 additions of cheese whey, and rebound sampling were conducted at treatment zone monitoring wells (TZMWs) which were impacted by cheese whey and at control zone monitoring wells (CZMWs), which were upgradient and downgradient of the treatment plot. The demonstration was conducted over a period of 696 days, including baseline sampling events.

The details of the treatability and site assessment work and of the complete experimental design and results are provided in the subsequent sections.

5.1 Laboratory Treatability Testing

5.1.1 Microcosms

Laboratory microcosm testing was performed to evaluate the most effective cosubstrates for promoting the biodegradation of explosive compounds in batch experimental systems prepared from soil collected from 157MW-5 (during installation of this monitoring well in December, 2004) and groundwater collected from 157MW-4. The cosubstrates evaluated were as follows: (1) lactate; (2) citrate; (3) benzoic acid; (4) yeast extract; (5) cheese whey, (6) hydrogen, (7) glucose, (8) acetate, and (9) ethanol. These cosubstrates were selected based on a literature review and previous laboratory and/or field studies conducted at Shaw to evaluate the degradation of explosives. The cost and potential field application of the cosubstrates was also considered.

For this screening-level study, site groundwater was initially spiked with 5 mg/L RDX, 1 mg/L HMX and 5 mg/L TNT. This spiking procedure was used to provide readily measurable concentrations of these contaminants in the microcosms. In the subsequent column studies (Section 5.1.2), the degradation of explosives at *in situ* concentrations was examined.

Microcosms were prepared by adding 100 mL of the spiked groundwater and 30 g of homogenized soil to thirty-six 160-mL serum bottles. Each cosubstrate was prepared in triplicate at a concentration of 5 mM, except for the yeast extract and cheese whey, which were prepared at a concentration of 500 mg/L, and the hydrogen, which was added to a final concentration of 3% in the headspace with 100 mg/L sodium bicarbonate (as a carbon source for autotrophic bacteria). One triplicate set of lactate-amended bottles was also amended with nutrients (35 μg/mL ammonia + 113 μg/mL phosphate). Controls consisted of a triplicate set of un-amended "Live" controls and a triplicate set of "Killed" controls, amended only with 1% formaldehyde to inhibit microbial activity.

After preparation, all serum bottles were sealed with Teflon-lined butyl rubber septa, and the headspace in each bottle was then flushed with at least 500 mL of nitrogen gas to remove residual oxygen. For treatments amended with hydrogen, 2 mL of hydrogen gas was injected into the bottle headspace immediately following the nitrogen flush. Microcosms were left to gently shake on their sides at 15^{o}C overnight. The next day, all microcosms were sampled for initial (time zero) explosives levels. Sampling was performed by removing a 1 mL sample through the septum using a 1 mL syringe equipped with a 25 ga. needle. Nitrogen gas was used to replace the volume removed. Samples were filtered through a 0.45 micron glass microfiber filter into pre-labeled 2 mL glass autosampler vials, which were then stored at 4°C until analyzed. For the remainder of the study, microcosms were incubated upside-down without shaking, and at 15^{o}C to simulate typical *in situ* groundwater temperatures at Picatinny Arsenal. Microcosms were sampled at 13, 27, 41, 55, 69, 89, and 152 days.

The concentrations of the parent explosives (RDX, HMX, TNT), initial RDX breakdown products (MNX, DNX, TNX) and initial TNT products (4-amino-2,6-DNT, 2-amino-4,6 DNT) in the groundwater were quantified using high performance liquid chromatography (HPLC) according to modified EPA Method 8330. The equipment used was a Hewlett-Packard Model 1100 HPLC (Agilent Technologies, Palo Alto, CA, USA) fitted with an autosampler, quaternary pump, Allure C18 reverse phase column (Restek Corporation, Bellefonte, PA, USA), and diode array detector (peak detection at 230 nm). The mobile phase was a 1:1 methanol:water (v:v) mixture at a flow rate of 0.9 ml/min. The effective detection limits for the analytes using this procedure are approximately 25 μg/L (without concentrating the sample), and using a 10-μL injection.

TNT was rapidly degraded in the presence of both cheese whey and yeast extract **(Figure 5.1)**. TNT levels were below detection in the microcosms that had been amended with cheese whey after 13 days, and TNT was below detection in the yeast extract-amended microcosms after 41 days. Interestingly, degradation of TNT was very slow in microcosms receiving simple carbon sources, such as glucose, lactate, and benzoate. In many soils, TNT is rapidly degraded with these substrates. RDX was also degraded in the presence of cheese whey and yeast extract, after a 55-day lag period and at a substantially slower rate than TNT **(Figure 5.2)**. RDX biodegradation in the presence of cheese whey was more rapid than in the presence of yeast extract, and after 152 days, over 98% of the RDX had been removed in the microcosms amended with cheese whey. The RDX breakdown products MNX and DNX, (but not TNX) were also formed in cheese whey and yeast extract-amended microcosms, with levels of both breakdown products first increasing, then decreasing as they were biologically degraded **(Figure 5.3)**. Other intermediates detected during RDX biodegradation included formaldehyde (which was transient) as well as methanol and nitrous oxide, which were terminal products, as expected from previous work (**Figure 1.1,** pathway A). Evidence of HMX biodegradation was first observed in the cheese whey-amended treatment after approximately 69 days of incubation, and after 152 days of incubation, 77% of the HMX had been removed from these microcosms **(Figure 5.4)**. Mono-, di-, tri-, and tetra-nitroso derivatives of HMX were detected at low concentrations **(Figure 5.5)**. As with RDX, methanol, formaldehyde, and nitrous oxide were also detected during the study, suggesting a similar reductive degradative route for HMX to that for RDX (**Figure 1.1**, pathway A).

Based on the initial microcosm screening, cheese whey and yeast extract were determined to be the most promising cosubstrates for treatment of the explosive compounds in Area 157 groundwater. None of the other cosubstrates tested appreciably stimulated explosives biodegradation. Based on this result, a column study was initiated to confirm the initial microcosm screening results and to better evaluate biodegradation kinetics of explosives at relevant field concentrations. Previous work in our laboratory suggests that flow-through aquifer columns may better simulate groundwater aquifers than batch microcosms, and that results from the two types of laboratory studies can sometimes differ (Schaefer et al., 2007).

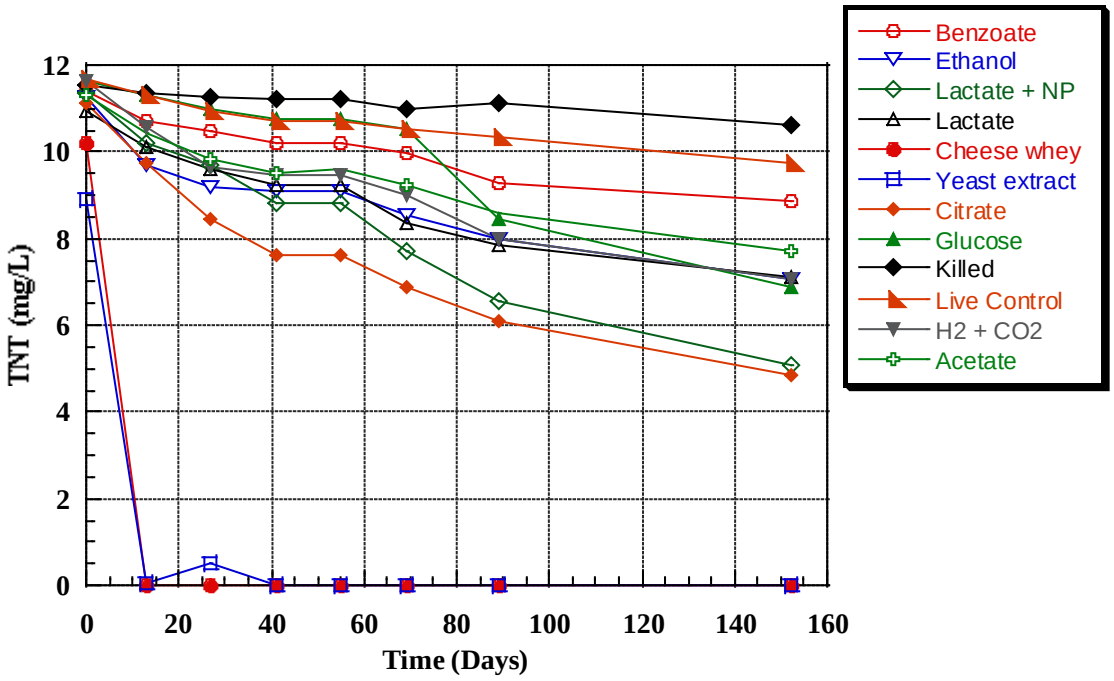


Figure 5.1. Biodegradation of TNT in Picatinny microcosms.

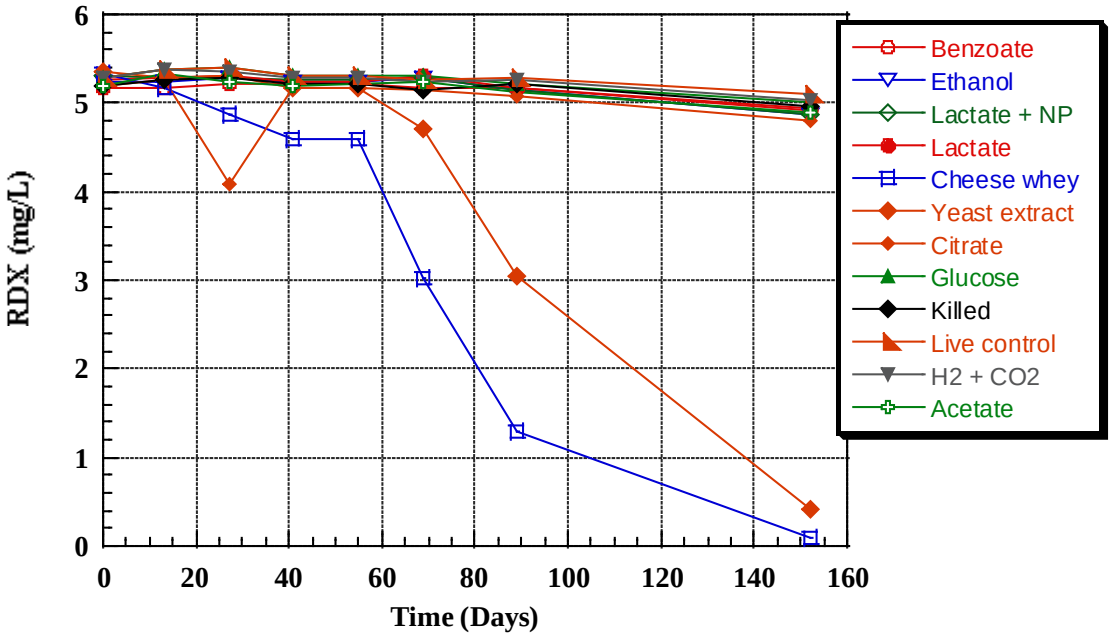


Figure 5.2. Biodegradation of RDX in Picatinny microcosms.

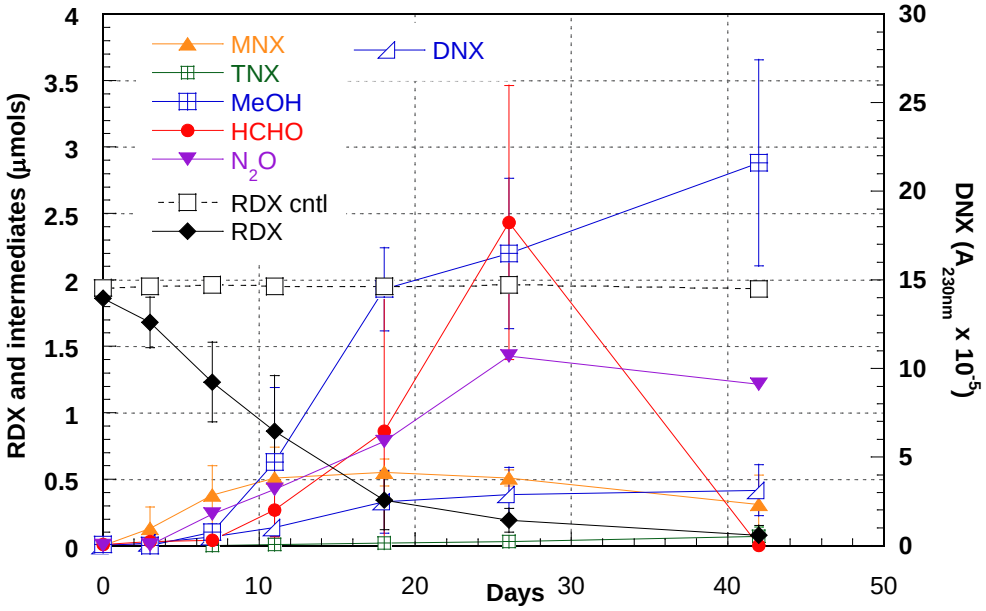


Figure 5.3. RDX biodegradation intermediates produced during incubation of Picatinny microcosms amended with cheese whey.

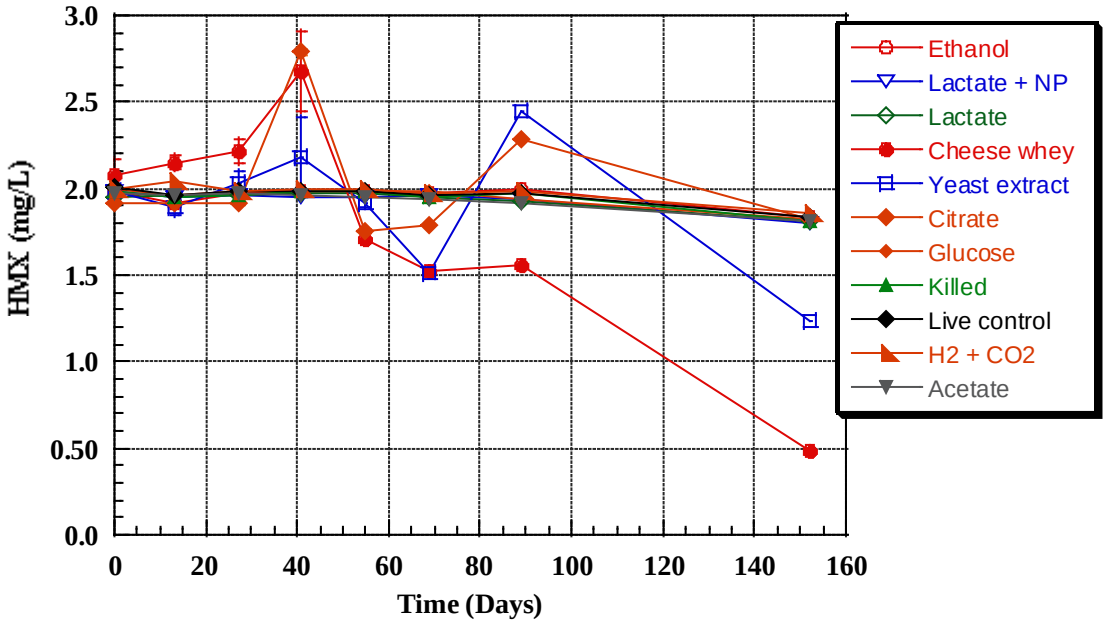


Figure 5.4. Biodegradation of HMX in Picatinny microcosms.

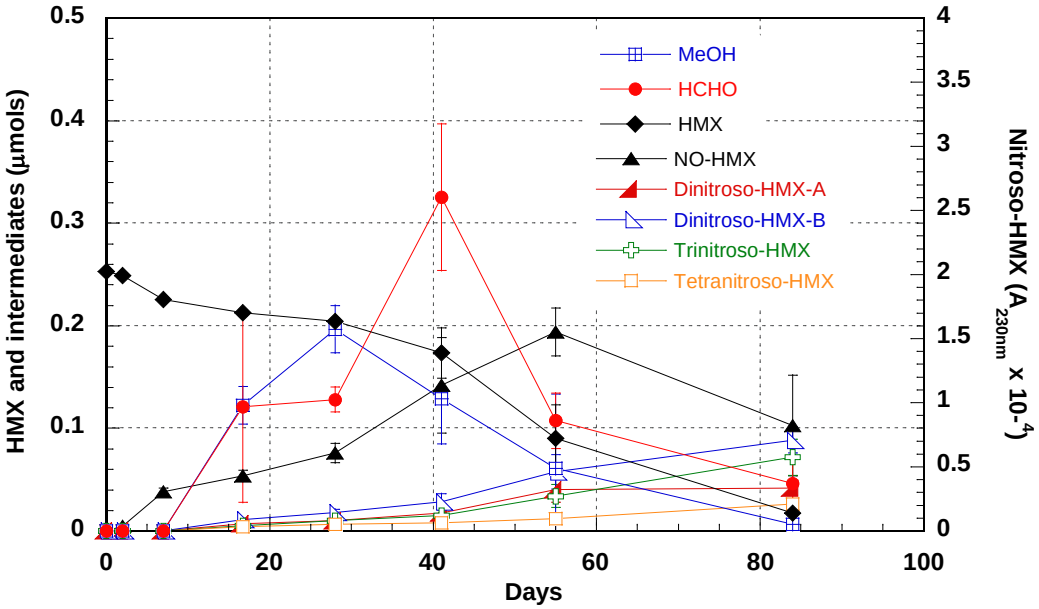


Figure 5.5. HMX biodegradation intermediates produced during Incubation of Picatinny microcosms amended with cheese whey.

5.1.2 Column Treatability Testing

Laboratory column tests were conducted to evaluate treatment effectiveness under more realistic aquifer conditions (i.e., aquifer sand matrix with flowing groundwater). Specifically, column treatability tests were used to determine the transport and kinetic parameters needed to develop the final conceptual design of the treatment system (conceptual system design is discussed in Section 5.3), and to confirm the microcosm data concerning the most effective cosubstrates for promoting energetic biodegradation at Picatinny. The column experiments were conducted with groundwater collected from MW-4 in Area 157 (roughly 40 to 80 μg/L each of TNT, RDX, and HMX).

Five laboratory columns, approximately 2.5 cm in diameter and 15 cm long, were constructed using PVC pipe with fitted end-caps. A detailed schematic of the column design is presented in **Figure 5.6** and a photograph is provided in **Figure 5.7**. A total of 106 to 131 g (dry wt) of homogenized site aquifer sediments from Area 157 were packed into each of the columns. Site groundwater was passed through each column at a flow rate of approximately 0.5 mL/hr using a syringe pump to approximate a 2-day hydraulic retention time (HRT). A bromide tracer test was initially performed on each column to quantify flow. Bromide (40 mL of 100 mg/L Br from NaBr) in groundwater was pumped through the columns at 0.5 mL/hour continuously. Fractions were collected from each column effluent and analyzed for Br using an ion selective electrode. At the completion of tracer testing, groundwater collected from well 157MW-4 was run for approximately 40 days through each column to allow influent and effluent explosives concentrations to stabilize. After the initial 40-day period, amendments were added to the columns as detailed below.

Five treatments were evaluated: (1) a "Killed" (abiotic) control that received 1% formaldehyde with the influent water to inhibit biodegradation; (2) a "Live" control that received groundwater but no amendments, (3) cheese whey-amended at 100 mg/L as total dissolved solids (TDS), cheese whey at 1,000 mg/L as TDS, and yeast extract-amended at 500 mg/L as TDS. The selection of cheese whey and yeast extract as cosubstrates was based on the results of the batch microcosm study as described in the previous section. The study was conducted at 15^{o}C for approximately 100 days after the bromide tracer experiments were complete. Explosives were analyzed in the influent and effluent of the columns by HPLC according to modified EPA method 8330 as previously described. Prior to analysis, the explosives were concentrated using solid phase extraction (SPE). During the concentration procedure, 50 mL of influent or effluent water was passed through a pre-treated SPE cartridge (Superclean ENVI Chrom P SPE Tubes, Supelco, Bellefonte, PA) under vacuum in a Vivi-Prep SPE Vacuum Manifold (Supelco) at 10 mL/min, and then dried thoroughly under vacuum. The SPE cartridge was then extracted with 4 mL of analytical grade acetonitrile, which was reduced under vacuum to ~ 1 mL using a Turbo-Vap II evaporator (Zymark, Hopkinton, MA). The extract was then placed in a GC vial and crimp-sealed with a Teflon-lined stopper. All analyses were conducted in the Shaw laboratory facility in Lawrenceville, NJ.

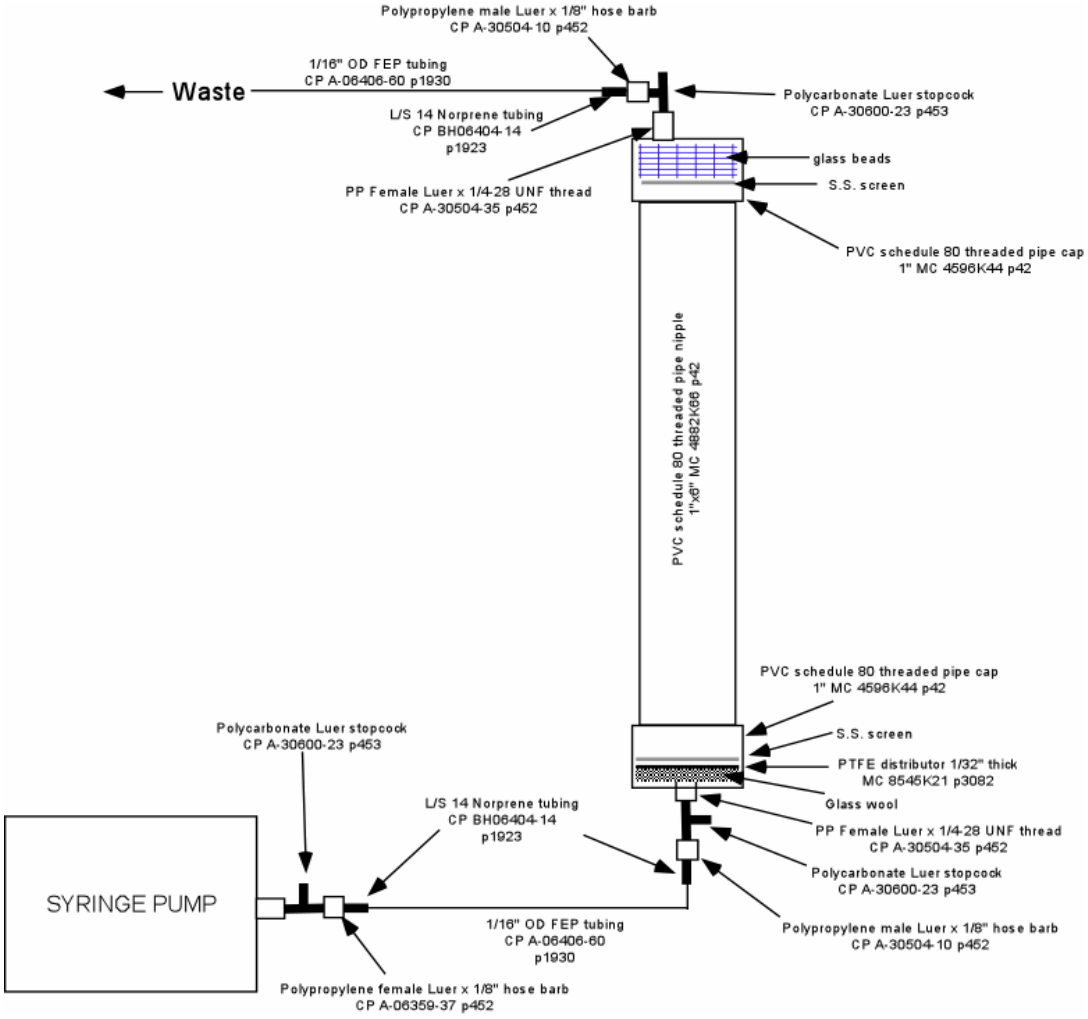


Figure 5.6. Schematic of column apparatus used to evaluate treatment effectiveness in bench-scale model aquifers.

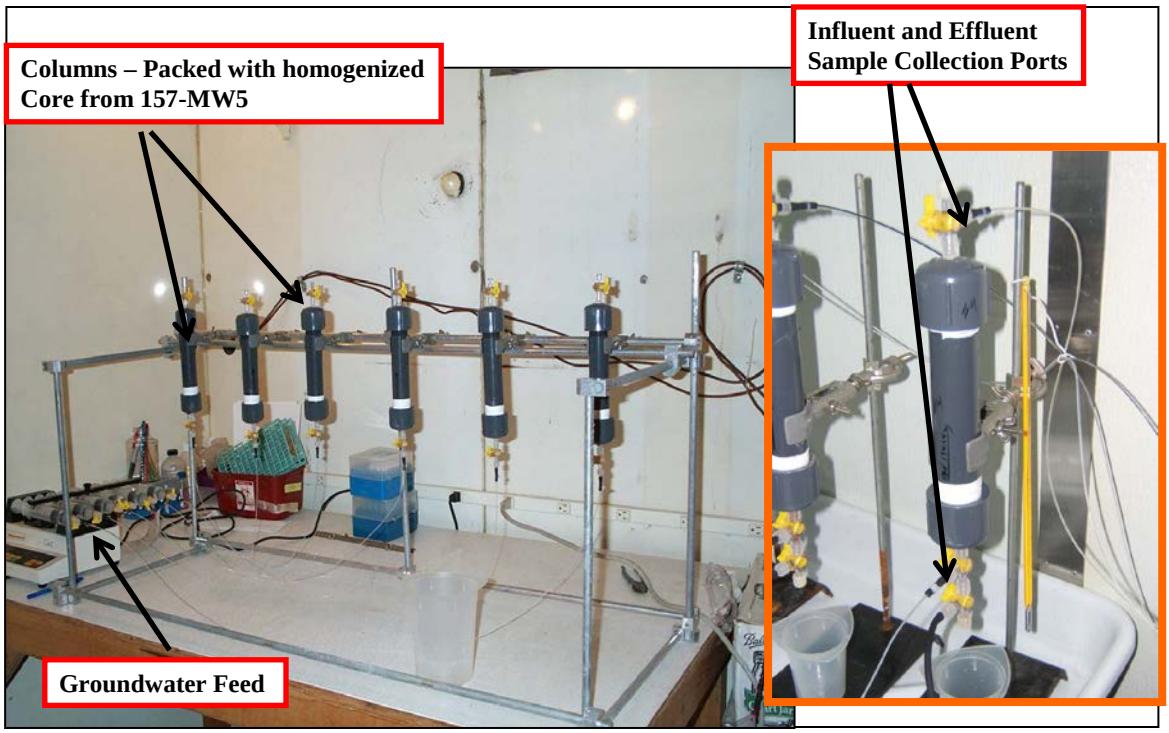


Figure 5.7. Photograph of model aquifer columns.

The bromide tracer tests conducted on the columns revealed that pore volumes ranged from ~ 26 to 31 mL **(Figure 5.8)**, which equates to a 54 h to 62 h HRT based on a 0.5 mL/h flow rate. During the initial 40 days of influent groundwater flow, concentrations of RDX and HMX in the influent and effluent water samples were similar, averaging ~ 50 µg/L (RDX) and 65 µg/L (HMX), respectively (**Figure 5.9** and **Figure 5.10**, respectively). The TNT concentrations in the influent and effluent showed significant variability during this time (**Figure 5.11**), but stabilized later in the study at ~ 45 µg/L. The source of this initial variability is unknown.

Over the ~ 100-day study, the most significant and consistent biodegradation of RDX and HMX occurred in the columns receiving cheese whey. RDX levels declined from ~ 50 µg/L to < 1 µg/L within 20-days of introducing the cosubstrate at 1000 mg/L **(Figure 5.9)**. Although the lag period was a little longer, HMX levels also declined from ~ 65 µg/L to < 1 ug/L in the effluent of this column **(Figure 5.10)**. This decline is appreciably greater than that observed in static microcosm studies **(Figure 5.4)**. In these studies, HMX appeared to degrade very slowly in the Area 157 sediments even with the addition of cheese whey. The time required to achieve reduction of RDX was slower in the column receiving 100 mg/L cheese whey, but concentrations < 1 µg/L were observed 35 days after cosubstrate was introduced and these concentrations were maintained. Rates of HMX degradation were slightly less in the columns with 100 mg/L cheese whey, with effluent levels stabilizing at ~ 5 µg/L at a ~ 2 day HRT. Yeast

extract also promoted degradation of both RDX and HMX, but the rates and extents of degradation of each of these explosives was less than observed with cheese whey at 100 or 1000 mg/L. Cheese whey and yeast extract each promoted the reduction in effluent TNT levels from ~ 50 μg./L to < 2 ug/L **(Figure 5.11)**. However, unlike RDX and HMX, TNT losses were also observed in the formaldehyde-killed and in the live control columns without cosubstrate added, with the latter column showing a somewhat greater reduction in effluent levels. The data suggest that both biotic and abiotic processes contributed to the decline in TNT concentrations across the column. Much of this reduction may reflect adsorption of the nitroaromatic explosive to the aquifer sediments. However, overall the data show that cheese whey at an initial concentration of 1000 mg/L promoted the most rapid and extensive degradation of all three target explosives. Moreover, the column results confirmed initial microcosm studies showing that cheese whey was an effective substrate for promoting biological reduction of RDX, and suggested that this cosubstrate will be effective in the field for HMX as well. Based on the laboratory studies, cheese whey was chosen as the cosubstrate for field injection.

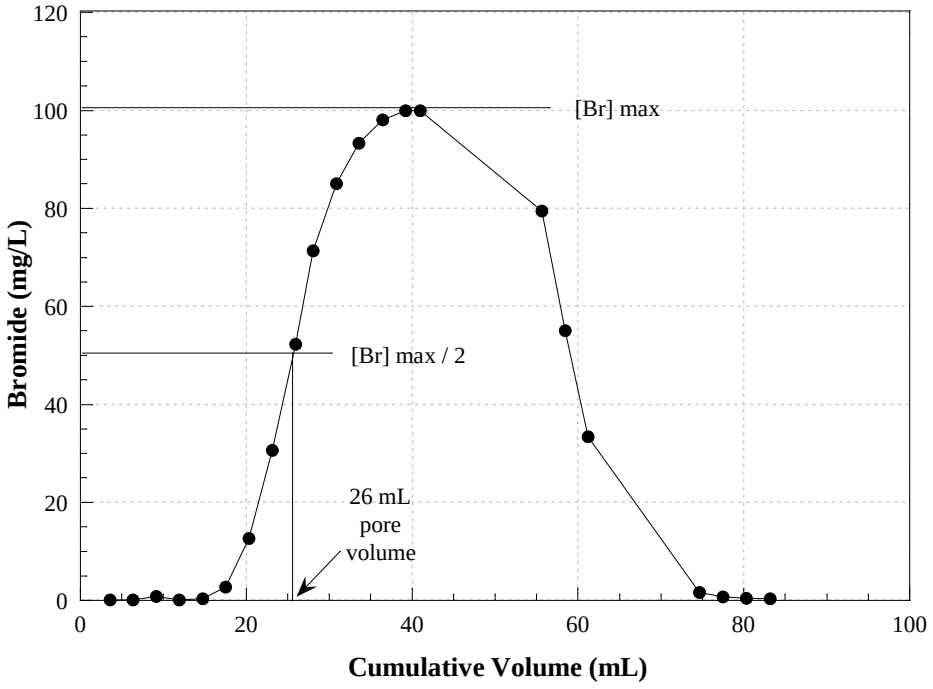


Figure 5.8. Typical bromide breakthrough curve for model aquifer column.
The pore volume for the 5 columns varied from 26 mL to 31 mL.

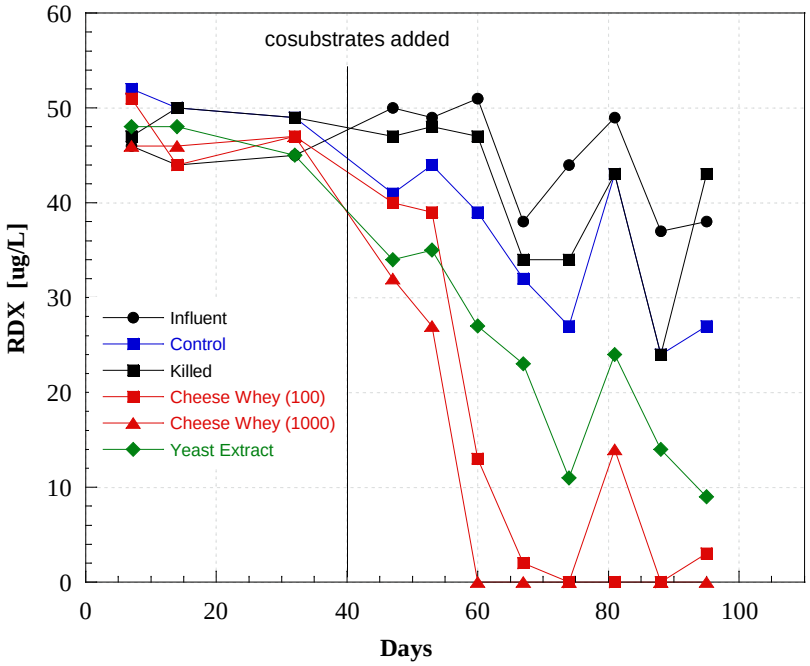


Figure 5.9 RDX concentrations in influent and effluent of aquifer columns. Co-substrate addition began on Day 40.

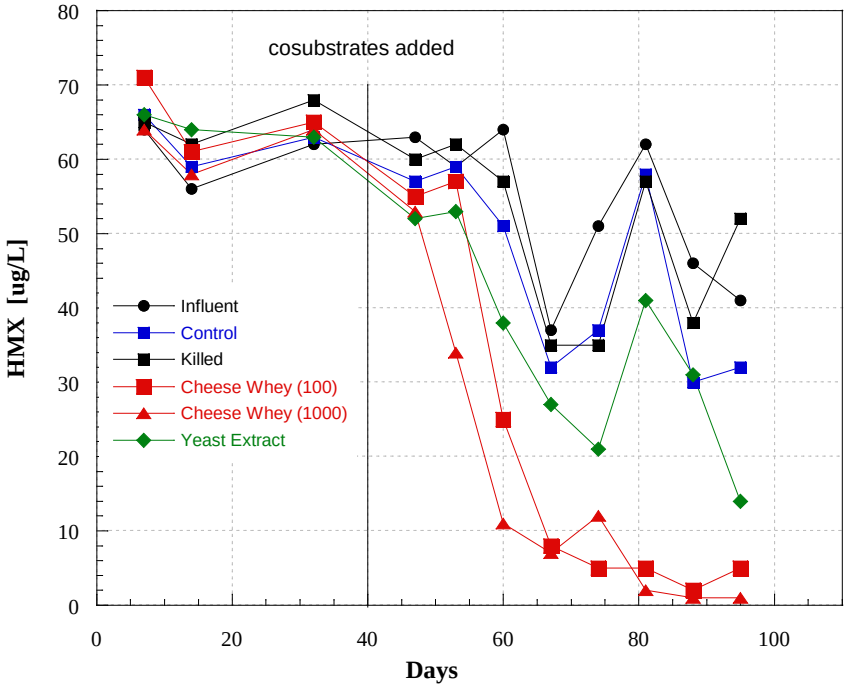


Figure 5.10 HMX concentrations in influent and effluent of aquifer columns. Co-substrate addition began on Day 40.

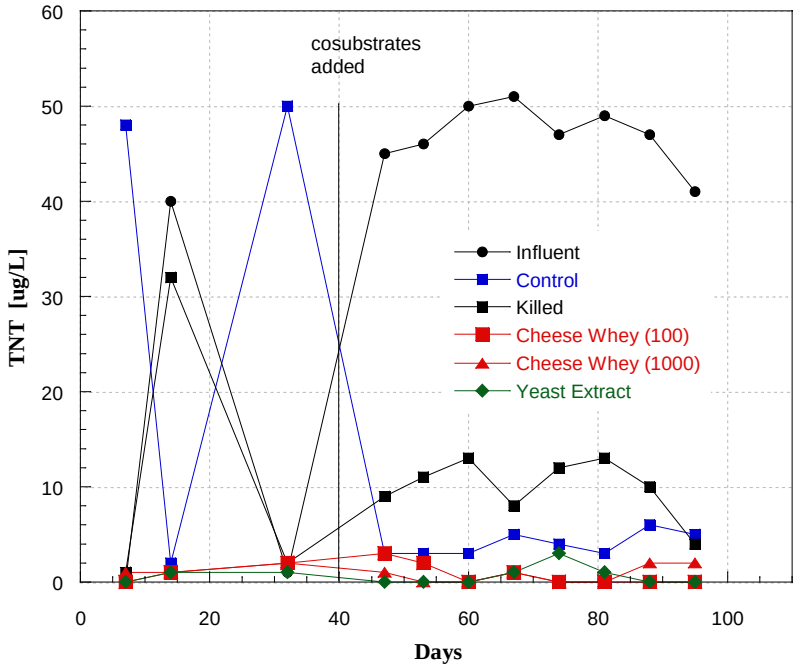


Figure 5.11. TNT concentrations in influent and effluent of aquifer columns. Co-substrate addition began on Day 40.

5.2 Site Characterization

After reviewing all previous soil, groundwater, and hydrogeological data from Area 157 (see Section 4), additional characterization work was conducted prior to completing the final design of the demonstration system, including monitoring well installation, soil and groundwater sampling, water elevation measurements, and slug and pump testing.

5.2.1 Monitoring Well Installation

An additional monitoring well, designated as 157MW-5, was installed in the target demonstration area adjacent to Building 823. The objectives of this well installation were as follows:

- Provide a monitoring point for performance of an aquifer pumping test (as described in Section 5.2.5);
- Verify hydraulic gradients and groundwater flow direction;
- Evaluate dissolved contaminant distribution;
- Serve as a performance monitoring well during treatment system operation;
- Collect aquifer samples for microcosm and column tests (see Section 5.1)

Installation of well 157MW-5 was performed during December, 2004. This well was installed using a hollow stem auger (HSA) drill rig, with a 4.25-inch drill bit, to a depth of 34.5-ft bgs. The monitoring well was constructed with 2-inch inner diameter, flush threaded, Schedule 40 PVC casing and factory slotted (0.010-inch) screen, with a screen interval of 24.5 to 34.5-ft bgs, and a solid PVC bottom cap. Clean silica sand (#1 size) was used in the filter pack around the well screen, which extends from the bottom of the well screen to five feet above the top of the screen (19.5 to 34.5-ft bgs). A 3-ft bentonite seal was installed from 16.5 to 19.5-ft bgs. The remaining annulus was sealed with a Portland cement/bentonite grout mixture and finished with a 4-inch flush mount cover with protective collar set in a concrete pad level with the surrounding terrain. Well construction details for 157MW-5, as well as all existing demonstration area test wells, are provided in Table 3.2. The location of this newly installed well is shown in Figure 3.6.

5.2.2 Groundwater Monitoring

5.2.2.1 Contaminant Data

Several groundwater sampling events were performed during the initial phase of this ESTCP Project to characterize site geochemical data and contaminant concentrations. On November 2-3, 2004, groundwater samples were collected from monitoring wells 157MW-1, 157MW-3, and 157MW-4 for geochemical and explosives analysis. Wells from Area 40 in Group 1 were also sampled at this time because this location was also being considered as a possible alternate demonstration site. Groundwater sampling at newly installed well 157MW-5 occurred on February 15, 2005. Each of these Area 157 wells was sampled again in May, 2005 during a more extensive site soil and groundwater investigation, as detailed in Section 5.2.3.

Groundwater samples were analyzed for energetic compounds (TNT, RDX, HMX, and their breakdown products) by Shaw's Analytical Laboratory in Lawrenceville, NJ and/or by Severn Trent Laboratories in Knoxville, TN using modified EPA Method 8330. The groundwater collected from the Area 157 monitoring wells had TNT concentrations ranging from below detection (below PQL of 0.5 μg/L) to 105 μg/L, RDX levels ranging from 15 μg/L to 68 μg/L and HMX concentrations ranging from 7.5 μg/L to 69 μg/L. In addition to these parent explosives, two TNT degradation products, 2-Amino-4,6-dinoitrotoluene (2A-4,6-DNT) and 4-amino-2,6-dinitrotoluene (4A-2,6-DNT) were detected in the wells at concentrations ranging from 3 μg/L to 51 μg/L. Trinitrobenzene (TNB) and 1,3,5-trinitrobenzene (1,3,5-TNB) were also detected at low concentrations in some wells. A summary of the analytical results from these wells is highlighted in **Table 5.1a and Table 5.1b**. This table also contains data from the May, 2005 Hydropunch investigation which is described in more detail in Section 5.2.3

Groundwater geochemical parameters, including pH, specific conductivity, dissolved oxygen, reduction potential, and temperature were measured in the field during sampling of the wells. These data are summarized in the highlighted section of **Table 5.2**. The pH of groundwater ranged from 5.2 to 6.2 in the Area 157 wells. Specific conductivity levels ranged from 0.12 to

0.24 μS/cm, dissolved oxygen levels ranged from 0.34 mg/L to 2.46 mg/L, and temperature ranged from 12.1°C to 12.8°C. The oxidation-reduction potential (ORP) was positive, varying from +88 to +294 mV. Groundwater samples from each well were also analyzed for anions, alkalinity, and pH by Shaw's Analytical Laboratory (summarized in **Table 5.3**). Alkalinity values in the wells varied from 13 to 28 mg/L, sulfate ranged from 14 mg/L to 26 mg/L, and chloride was between 9 and 63 mg/L. Nitrate, nitrite, bromide and phosphate concentrations were below the PQL of 0.1 mg/L by EPA method 300.0 in each of the monitoring wells.

5.2.2.2 Groundwater Depth, Hydraulic Gradient, and Flow Direction

In addition to the groundwater monitoring events in November 2004 and February 2005, depth-to-water was measured in monitoring wells 157MW-1, 157MW-1D, 157MW-2, 157MW-3, 157-MW-4, and 157-MW5 in December, 2004, April, 2005 and May, 2005. These data were collected in order to measure the water table elevation (and elevation changes with time), and ultimately to determine the hydraulic gradient and flow direction. Groundwater contours based on these five synoptic events are shown in **Figures 5.12a-5.12e**. Results indicate that the horizontal hydraulic gradient is relatively flat (approximately $1x10^{-4}$ ft/ft), with a flow direction that varies but generally trends between southeast and southwest. Using deep bedrock monitoring well 157MW-1D, which is screened approximately 100 ft deeper than the other Area 157 monitoring wells, the vertical hydraulic gradient is approximately $4x10^{-3}$ ft/ft downwards. Comparison of these gradients suggests that there may be a substantial component of downward flow at the Area 157 site. Based on these findings, the deep bedrock well 157MW-1D was monitored throughout the demonstration to determine if any explosives were transported downward to due to the groundwater recirculation at the demonstration plot. No downward migration of contamination to the deep well was observed during the course of the study.

Table 5.1a. Explosives Concentrations in Area 157 Monitoring Wells and in Hydropunch Samples.

Field Sample	Date Sampled	Sample Depth	COMPOUND						
		(ft bgs)	TNT	2,4-DNT	2,6-DNT	2A-4,6-DNT	4A-2,6-DNT	RDX	HMX
157HP-6A	5/4/2005	10-12	**12.7**	ND	**32**	**94**	ND	**378**	**103**
157HP-6B	5/4/2005	30-32	ND	ND	ND	**2.8**	ND	**8.4**	**9.9**
157HP-6C	5/4/2005	44-46	ND	ND	**1.7**	**4.8**	ND	**7.9**	**8.2**
157HP-7A	5/4/2005	10-12	**321**	ND	**87**	ND	ND	**1072**	**69**
157HP-7B	5/4/2005	30-32	ND	ND	ND	ND	ND	ND	ND
157HP-7C	5/4/2005	44-46	ND	ND	ND	**1.8**	ND	**20**	**7.2**
157HP-8A	5/4/2005	10-12	ND	ND	ND	**3.1**	ND	**16**	**19**
157HP-8B	5/4/2005	30-32	**6.5**	ND	**17.5**	**17**	ND	**33**	**32**
157HP-8C	5/4/2005	44-46	ND	ND	**2.6**	**4.3**	ND	**6.1**	**4.4**
157MW-1	11/3/2004	24-34	ND	**0.26**	ND	**3.4**	**3.3**	**22**	**7.5**
157MW-3	11/3/2004	26.5-36.5	ND	**0.81**	ND	**15**	**21**	**15**	**13**
157MW-4	11/2/2004	24-34	ND	ND	ND	**25**	**27**	**68**	**69**
157MW-5	2/15/2005	24.5-34.5	**105**	ND	**43**	**51**	ND	**59**	**68**

ND = Non detect

Concentrations in μg/L.

Only explosive compounds that were detected are listed.

Table 5.1b. Explosives Concentrations in Area 157 Monitoring Wells and in Hydropunch Samples.

Field Sample	Date Sampled	Sample Depth	COMPOUND						
		(ft bgs)	DNX	MNX	TNX	NB	TNB	1,3,5-TNB	1,3-DNB
157HP-6A	5/4/2005	10-12	ND	ND	ND	ND	ND	ND	ND
157HP-6B	5/4/2005	30-32	ND	ND	ND	ND	**39**	ND	ND
157HP-6C	5/4/2005	44-46	ND	ND	ND	**13**	**33**	ND	ND
157HP-7A	5/4/2005	10-12	**4.9**	**18**	**3.2**	ND	**12**	ND	ND
157HP-7B	5/4/2005	30-32	ND	ND	ND	ND	ND	ND	ND
157HP-7C	5/4/2005	44-46	ND	ND	ND	ND	ND	ND	ND
157HP-8A	5/4/2005	10-12	ND	ND	ND	ND	ND	ND	ND
157HP-8B	5/4/2005	30-32	ND	ND	ND	ND	**36**	ND	ND
157HP-8C	5/4/2005	44-46	ND	ND	**3.1**	ND	**74**	ND	ND
157MW-1	11/3/2004	24-34	ND	ND	ND	ND	ND	**15**	**0.22**
157MW-3	11/3/2004	26.5-36.5	ND	ND	ND	ND	ND	**10**	ND
157MW-4	11/2/2004	24-34	ND	ND	ND	ND	ND	**26**	ND
157MW-5	2/15/2005	24.5-34.5	ND	ND	ND	ND	**17**	ND	ND

Table 5.2. Field Geochemical Parameters for Area 157 Monitoring Wells and Hydropunch Locations.

Field Sample	Date Sampled	Sample Depth (ft bgs)	GW Field Parameters						
			Temp (^{o}C)	Conductivity (mS/cm)	DO (%)	DO (mg/L)	pH (SU)	Redox (mV)	Turbidity (NTU)
157HP-6A	05/04/05	10-12	8.22	0.176	0.00	0.00	6.6	51.0	68
157HP-6B	05/04/05	30-32	11.89	0.293	0.03	0.00	5.4	98.5	1030
157HP-6C	05/04/05	44-46	11.76	0.280	1.6	0.17	5.9	65.4	528
157HP-7A	05/04/05	10-12	8.17	0.094	2.1	0.25	6.6	58.3	27.2
157HP-7B	05/04/05	30-32	10.74	0.185	2.6	0.29	6.1	51.2	956
157HP-7C	05/04/05	44-46	10.81	0.186	5.8	0.63	6.5	32.2	996
157HP-8A	05/04/05	10-12	8.17	0.049	0.7	0.05	6.4	41.5	286
157HP-8B	05/04/05	30-32	11.01	0.139	18.5	1.94	6.1	56.5	1369
157HP-8C	05/04/05	44-46	11.71	0.157	50	5.42	6.3	26.9	1290
157MW-1	11/03/04	24-34	12.85	0.242	3.3	0.34	5.2	294	0.8
157MW-3	11/03/04	26.5-36.5	12.17	0.173	13.1	1.41	5.7	251.5	0.0
157MW-4	11/02/04	24-34	12.10	0.117	22.9	2.46	6.2	216.8	4.1
157MW-5	02/15/05	24.5-34.5	10.89	0.179	8.2	0.90	6.2	216.6	7.1
157MW-5	05/02/05	24.5-34.5	11.20	0.177	10.7	1.17	5.9	87.8	5.7

Table 5.3. Laboratory Geochemical Parameters for Area 157 Monitoring Wells and Hydropunch Locations.

Field Sample	Chloride (mg/L)	Sulfate (mg/L)	Nitrite (mg/L)	Phosphate (mg/L)	Bromide (mg/L)	Nitrate (mg/L)	Alkalinity (mg/L)	pH (SU)
157HP-6A	13.0	12.4	<0.1	<0.1	<0.1	<0.1	59.7	6.5
157HP-6B	52.6	20.2	<0.1	<0.1	<0.1	0.2	20.4	5.6
157HP-6C	50.9	18.4	<0.1	<0.1	<0.1	0.6	17.3	5.6
157HP-7A	1.9	4.5	<0.1	<0.1	<0.1	0.2	38.2	5.9
157HP-7B	28.9	15.5	<0.1	<0.1	<0.1	0.2	22.0	5.8
157HP-7C	26.4	16.1	<0.1	<0.1	<0.1	0.1	22.0	6.0
157HP-8A	2.9	6.2	<0.1	<0.1	<0.1	<0.1	9.4	5.6
157HP-8B	16.3	15.2	<0.1	<0.1	<0.1	<0.1	20.4	5.8
157HP-8C	20.5	15.9	<0.1	<0.1	<0.1	<0.1	16.2	5.9
157MW-1	63.0	26.9	<0.1	<0.1	<0.1	<0.1	12.6	5.2
157MW-3	30.6	26.3	<0.1	<0.1	<0.1	<0.1	28.3	5.7
157MW-4	8.9	14.5	<0.1	<0.1	<0.1	<0.1	36.7	6.2
157MW-5	20.7	15.0	<0.1	<0.1	<0.1	<0.1	28.3	6.0

Groundwater samples from were collected on 5/4/05-5/5/05, except for 157MW-1, 157MW-3, and 157MW-4, which were taken on 12/20/04.

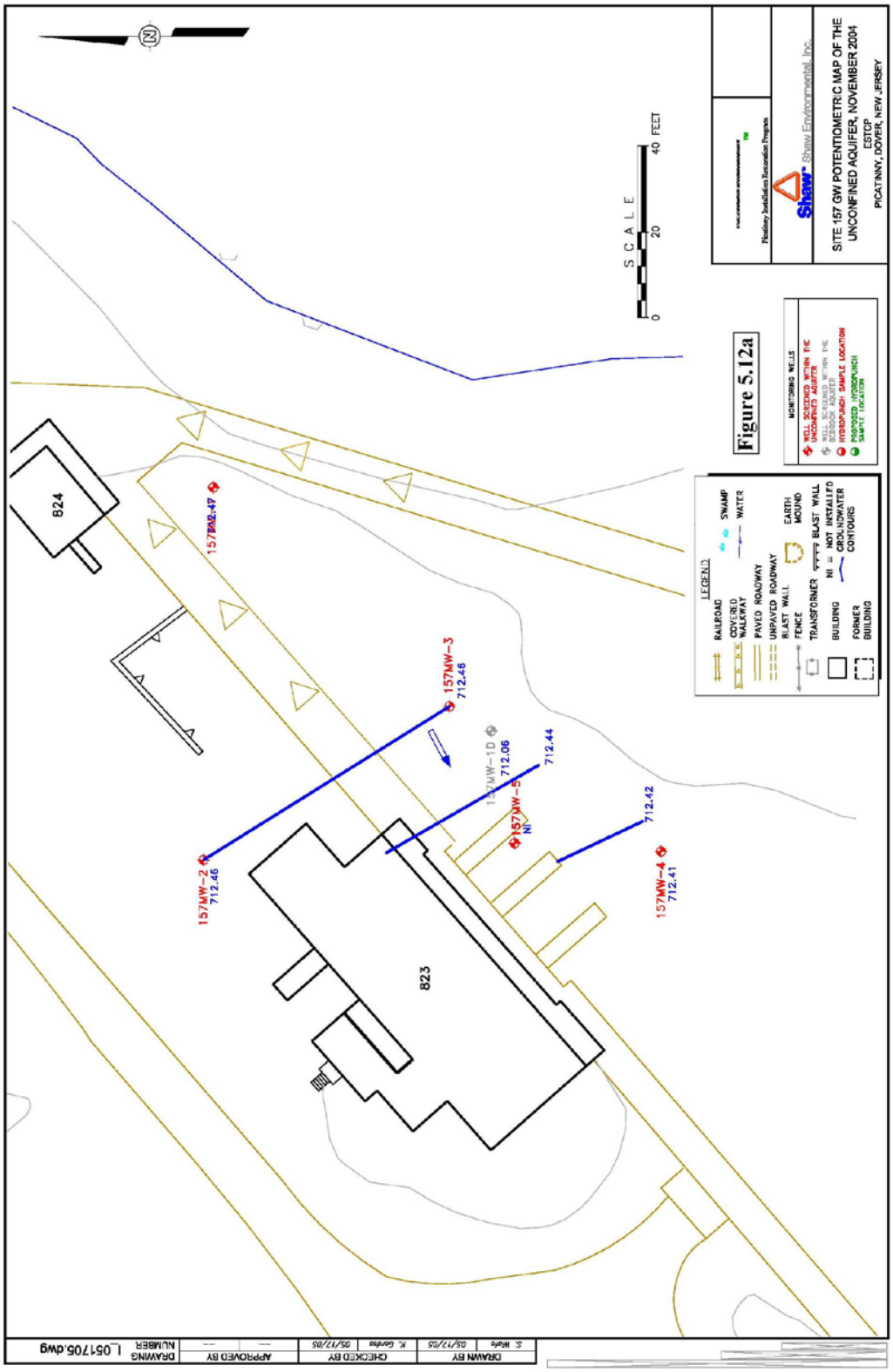


Figure 5.12a. Area 157 potentiometric map of the unconfined aquifer, November, 2004.

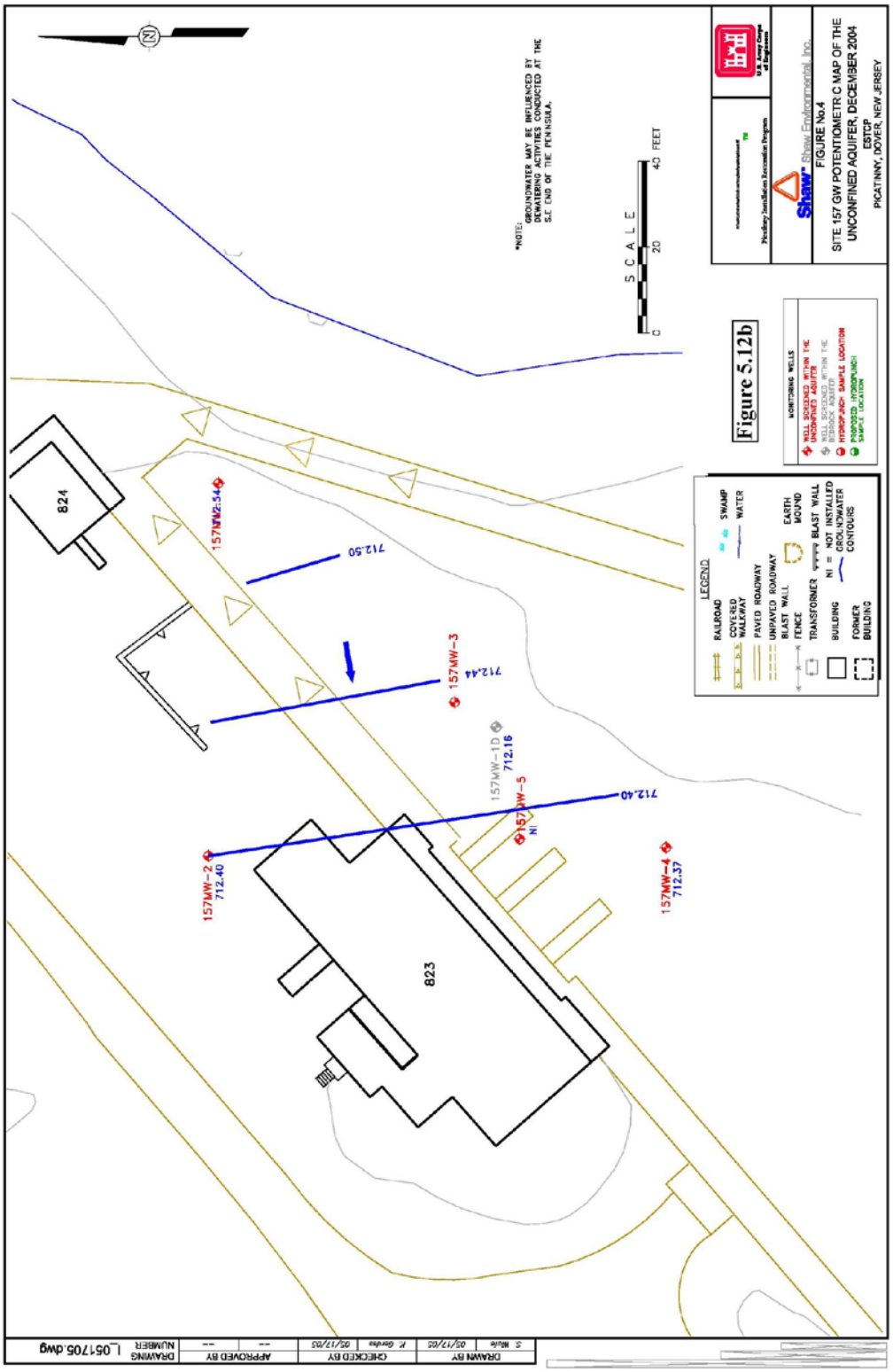


Figure 5.12b. Area 157 potentiometric map of the unconfined aquifer, December, 2004.

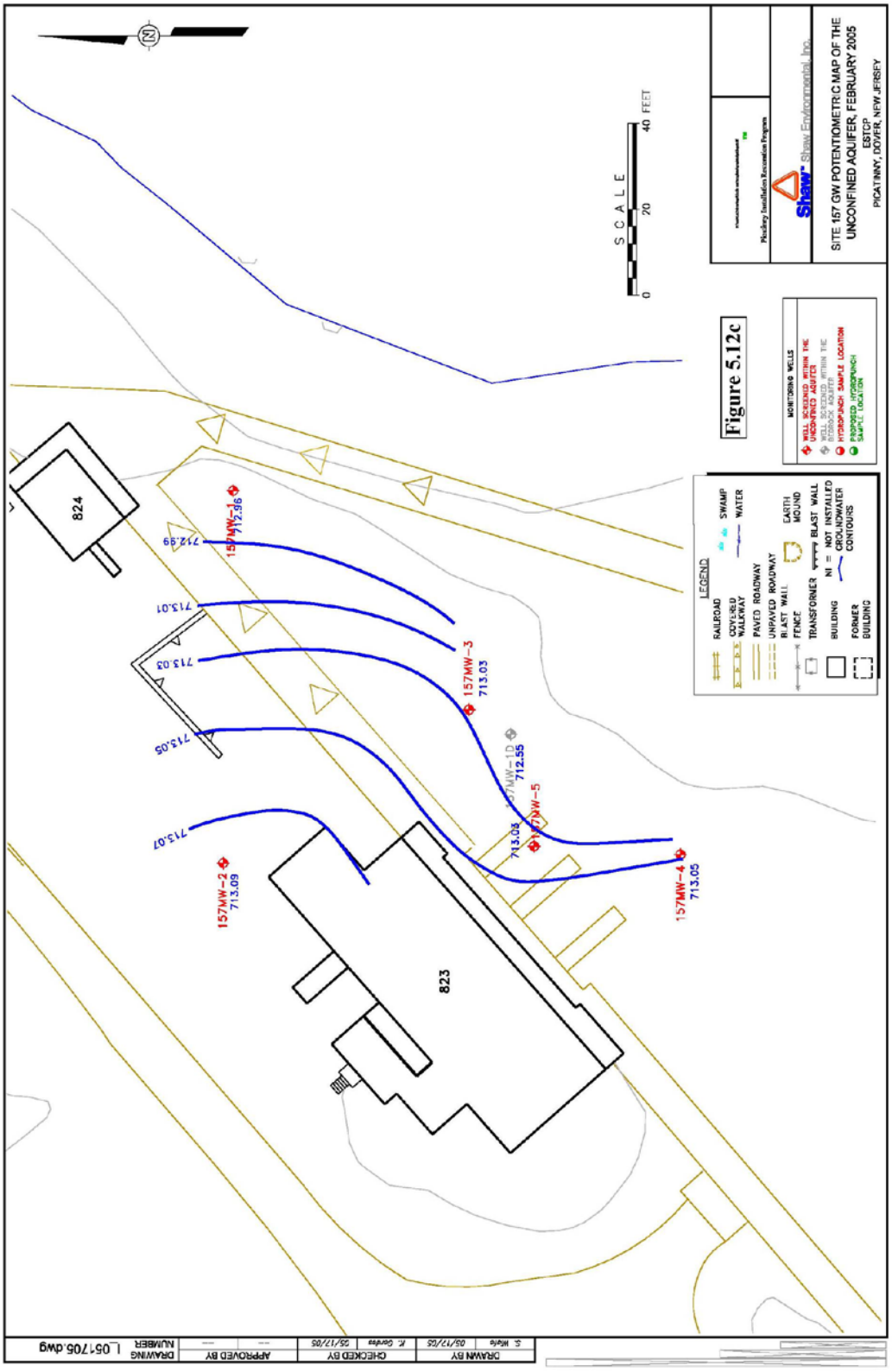


Figure 5.12c. Area 157 potentiometric map of the unconfined aquifer, February, 2005.

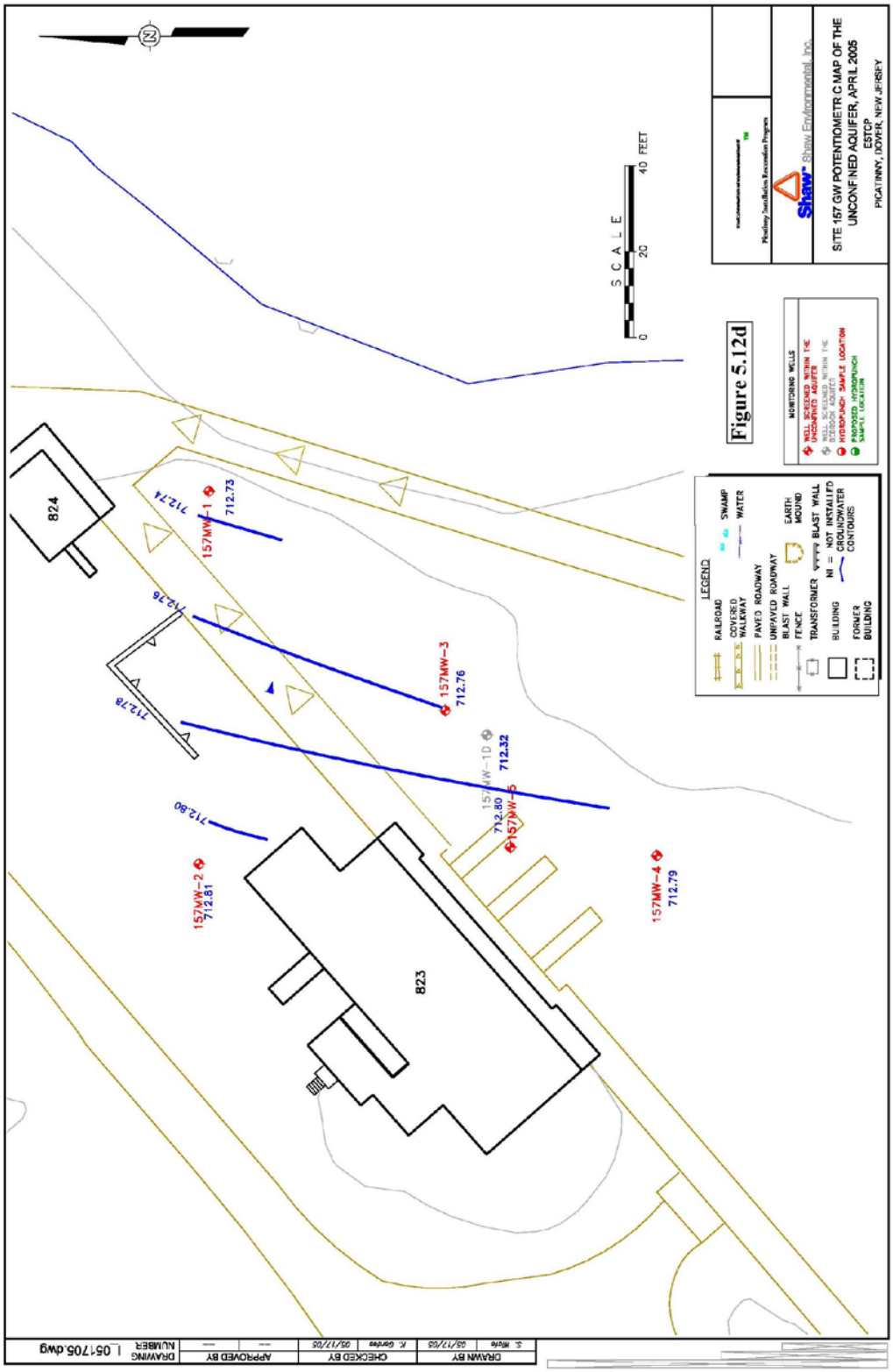


Figure 5.12d. Area 157 potentiometric map of the unconfined aquifer, April, 2005.

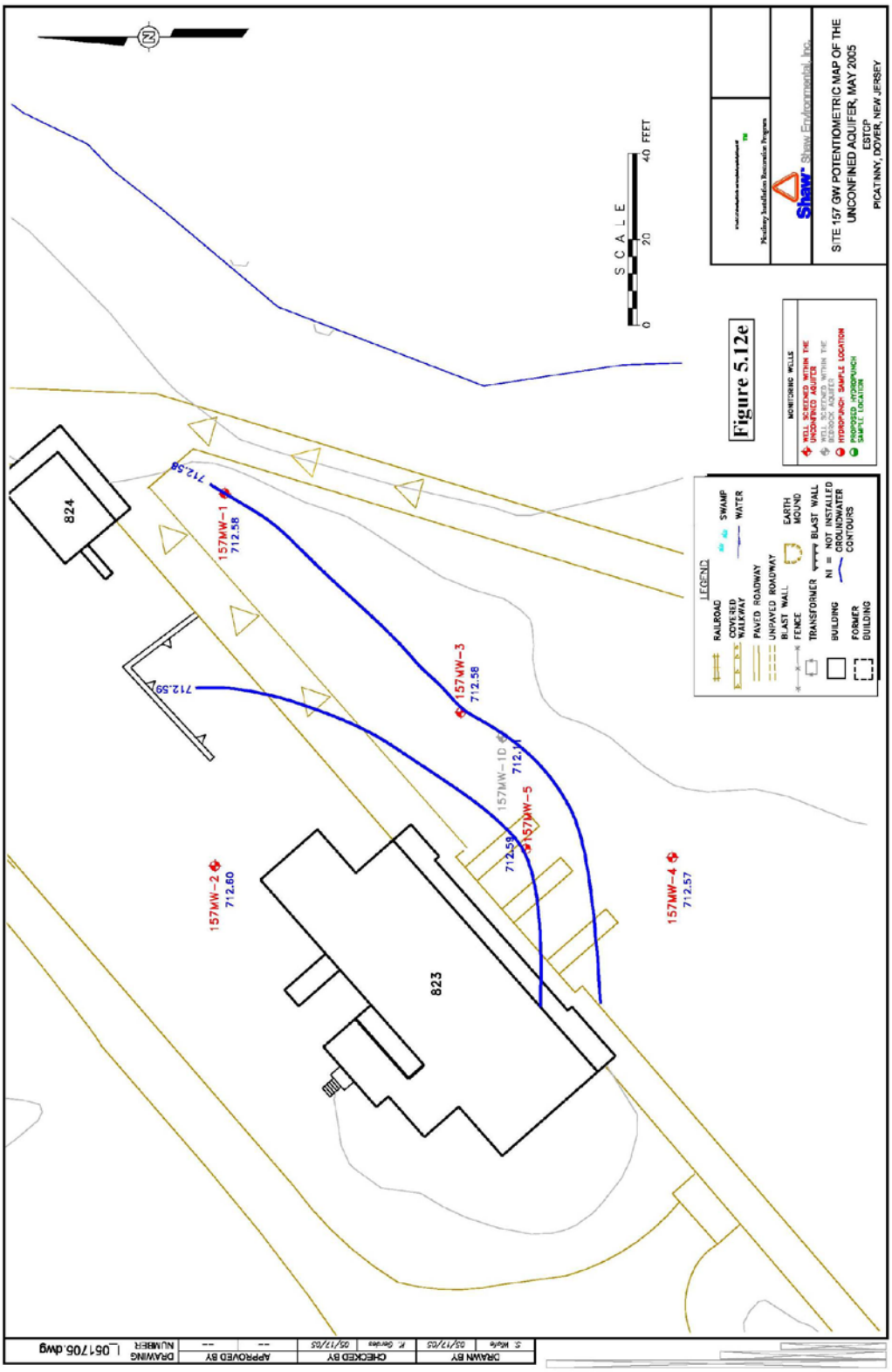


Figure 5.12e. Area 157 potentiometric map of the unconfined aquifer, May, 2005.

5.2.3 Groundwater and Surface Soil Investigation

5.2.3.1 Surface Soil Sampling and Hydropunch Investigation

Based on historical soil and groundwater data, as well as the groundwater data collected during the monitoring described in Section 5.2.2, a limited groundwater and surface soil investigation was performed to improve delineation of the dissolved contaminant plume and identify potential source areas. This information was needed in order to properly design and orient the *in situ* biological treatment barrier.

Surface soils were sampled by hand at a depth of approximately 1 ft. bgs at nine locations throughout Area 157 on May 2, 2005. The locations were chosen based on a review of previous data and discussions with site personnel. Most of the locations selected were adjacent to Building 823 in areas were historic surface releases of explosives-contaminated wastewater may have occurred. Soil sample locations are identified in **Figure 4.6**. The concentrations of explosives found during the soil sampling event are summarized in **Table 5.2**. The highest concentrations of RDX and HMX in soil were found at sample locations 157SS-12 (RDX; 1254 mg/kg and HMX; 258 mg/kg) and 157SS-13 (RDX; 13 mg/kg and HMX; 2.5 mg/kg) on the north side of Building 823. Soil contamination was also observed in this area at one location during previous investigative work (Sample 157SB-1A in **Figure 4.9**). Approximately 36 mg/kg of RDX was detected during this sampling event. The limited soils data from this region indicate that there may be one or more potential contaminant sources located on the north side of Building 823. Based on groundwater flow, this soil contamination may be contributing to the dissolved energetic compounds observed in the Area 157 groundwater. However, elevated RDX and TNT concentrations were also measured previously in soil at 157SS-7 and RDX was detected at 157SS-3C (**Figure 4.9**). These samples were taken along the drainage lines running east (and slightly north) from Building 823 to Picatinny Lake. Although a surface soil sample collected from this region was relatively clean (**Table 5.4**, sample 157SS-11), a shallow Hydropunch sample taken subsequently showed elevated levels of RDX, HMX, TNT, 2,6-DNT, and 2A-4,6DNT (**Table 5.1a**, sample 157HP-6a). The Hydropunch technique and resulting data are discussed in more detail below. However, the limited soil sampling suggested that surface soil contamination may be present in at least two if not more regions throughout Area 157 rather than in one discreet source area.

Concurrent with the soil investigation, a Hydropunch groundwater investigation was performed on May 4th and 5th, 2005. The Hydropunch is a direct-push device that is designed to collect discreet groundwater samples without installation of a permanent or temporary monitoring well. Using this approach, groundwater samples were collected from three boring locations at three depth intervals: 10 to 12 ft. bgs (just below the water table), 30 to 32 ft. bgs (within the well screen interval of 157MW-1 through 5), and 44 to 46 ft. bgs. The Hydropunch was advanced using a Geoprobe. Upon reaching each groundwater sampling depth interval, the drive point in the Hydropunch was disengaged, exposing a stainless steel screen to the formation in an

increment of approximately 2-ft. A peristaltic pump connected to polyethylene tubing was used to obtain samples from the various depths. Each sample was collected after allowing groundwater to purge for several minutes to minimize turbidity. Sample locations are shown in **Figure 4.6**.

Contaminant and geochemical results of the May, 2005 Hydropunch investigation are summarized in **Table 5.1a, Table 5.1b** and **Table 5.2**, respectively. These tables also contain data from monitoring wells sampled on these dates, which was discussed previously in this chapter. Plan and cross-sectional views of RDX groundwater concentration contours based on relevant sampling data (Hydropunch and monitoring wells) are provided in **Figures 5.13a-5.13c**. Plan and cross-sectional views of TNT groundwater concentration contours are provided in **Figures 5.14a-514c**. Contaminant concentration contours derived from the Hydropunch and monitoring well data are consistent with the presence of soil sources near Building 823, as the dissolved contaminant plume appears to emanate and migrate downgradient from this area. In addition, Hydropunch data indicate that groundwater contaminant concentrations generally decrease with depth, which is consistent with a shallow soil source within Area 157. Groundwater data collected from the shallow depth interval at 157HP-7 are consistent with the presence of explosive compound soil sources located adjacent to the northern half of Building 823, suggesting that groundwater is impacted by contaminants present within the unsaturated zone and shallow soils. Elevated contaminant concentrations in the shallow depth interval of 157HP-6 suggest that contaminant sources in shallow soils may also reside near the covered walkway, south of Building 824. An additional Hydropunch investigation to improve vertical delineation of RDX was subsequently conducted as discussed in Section 5.2.3.2.

Groundwater contours indicate that the dissolved plume is migrating downwards as the plume migrates laterally downgradient from the suspected source areas, which is consistent with the observed vertical hydraulic gradients (discussed previously in Section 5.2.2.2). Thus, the *in situ* treatment system was designed to serve as a barrier to mitigate both the horizontal and vertical migration of dissolved contaminants, as groundwater treatment was targeted in the “core” of this plume. Additional discussion of the location and depth interval of the treatment system is presented in Section 5.3

Table 5.4. Soil Analytical Results from Sampling Performed in May, 2005.

Field Sample	Date Sampled	Sample Depth	Compound						
			RDX	HMX	MNX	Tetryl	TNT	2,6-DNT	2A-4,6-DNT
157SS-11	05/02/05	0-1	ND	ND	ND	ND	ND	ND	**0.08**
157SS-12	05/02/05	0-1	**1254**	**258**	**1.01**	ND	**15**	**4.8**	**3.0**
157SS-13	05/02/05	0-1	**13**	**2.5**	ND	ND	**2.3**	**1.3**	**1.2**
157SS-14	05/02/05	0-1	ND	ND	ND	ND	ND	**0.20**	**0.15**
157SS-15	05/02/05	0-1	ND	**0.53**	ND	ND	ND	**0.18**	**0.13**
157SS-16	05/02/05	0-1	ND	ND	ND	ND	ND	ND	ND
157SS-17	05/02/05	0-1	ND	ND	ND	ND	ND	ND	ND
157SS-18	05/02/05	0-1	ND	ND	ND	ND	ND	ND	ND
157SS-19	05/02/05	0-1	**0.33**	ND	ND	**1.2**	**36**	ND	**0.11**

ND = Non detect

Only explosive compounds that were detected are listed.

value listed is the highest value detected in replicate samples

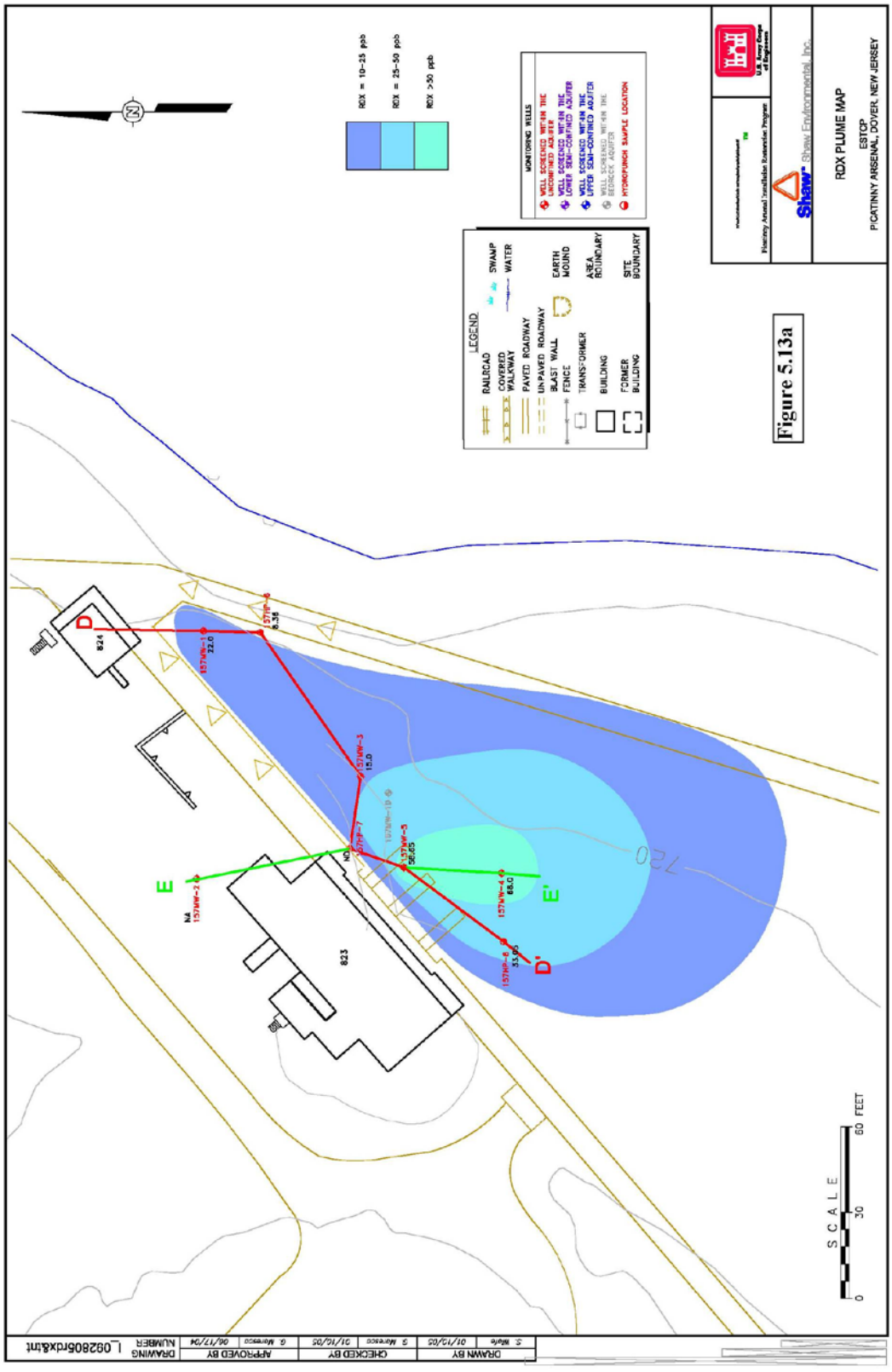


Figure 5.13a. Overhead view of RDX plume in Area 157.

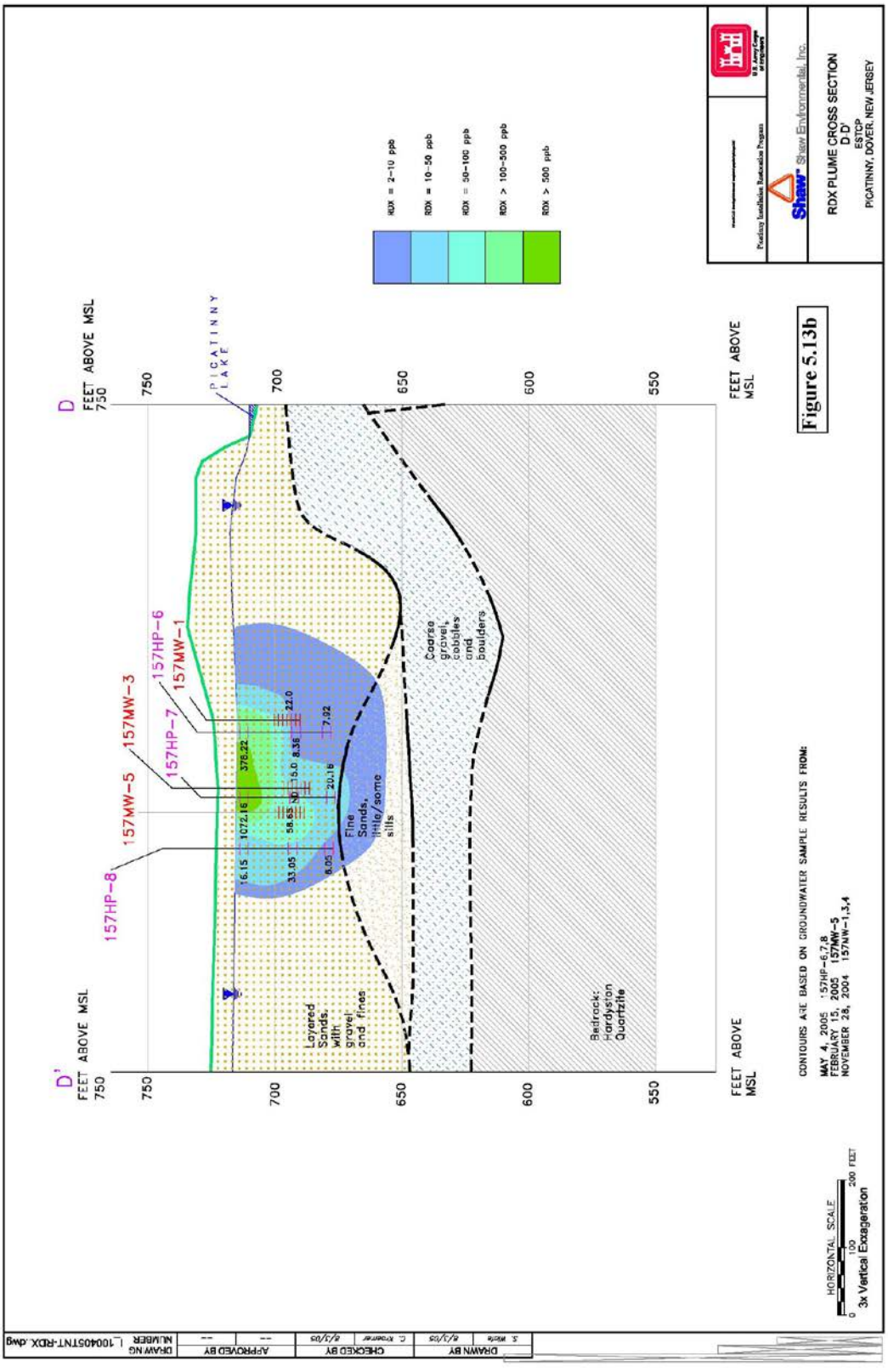


Figure 5.13b. RDX plume cross section D-D'.

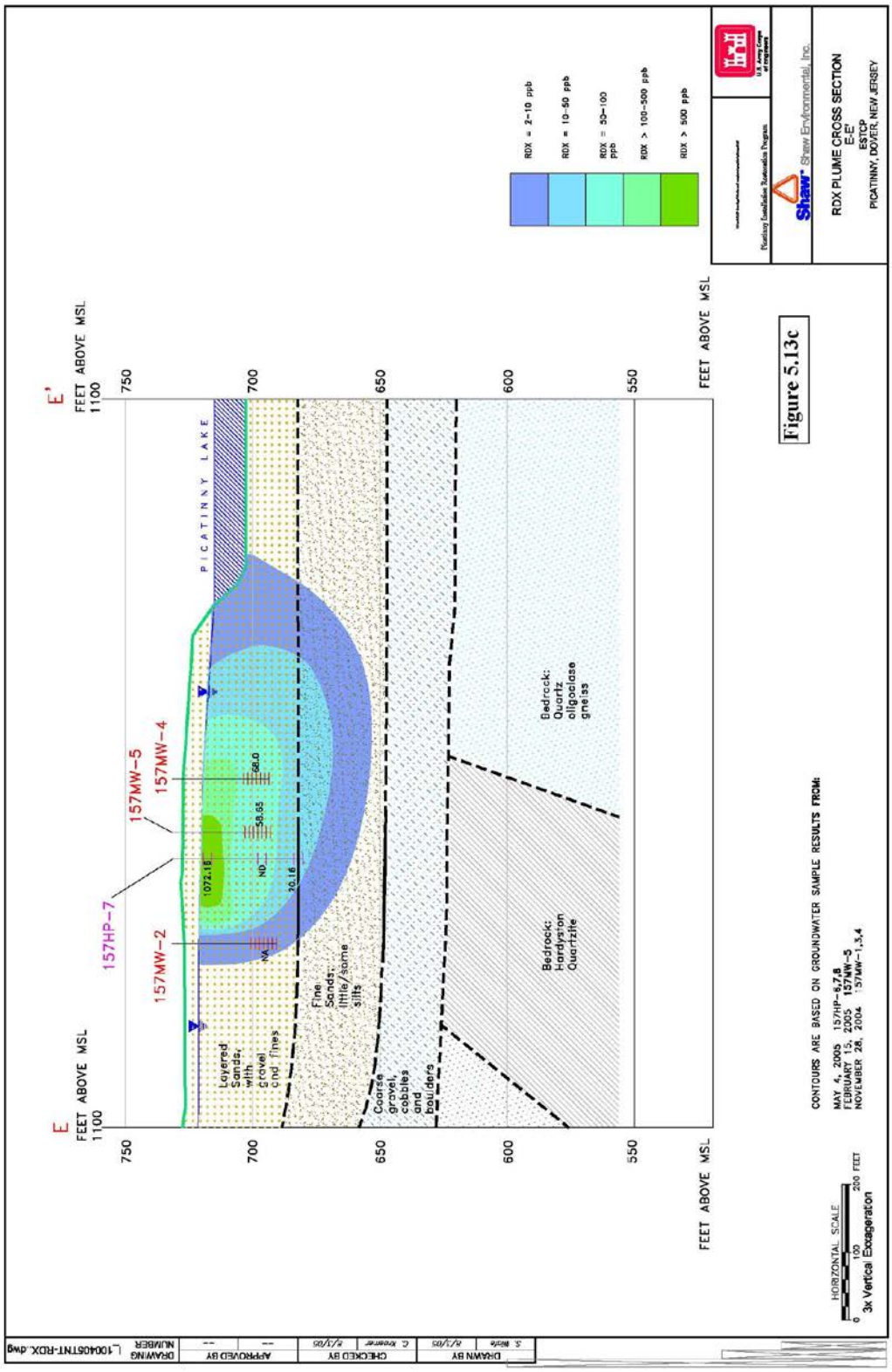


Figure 5.13c. RDX plume cross section E-E'.

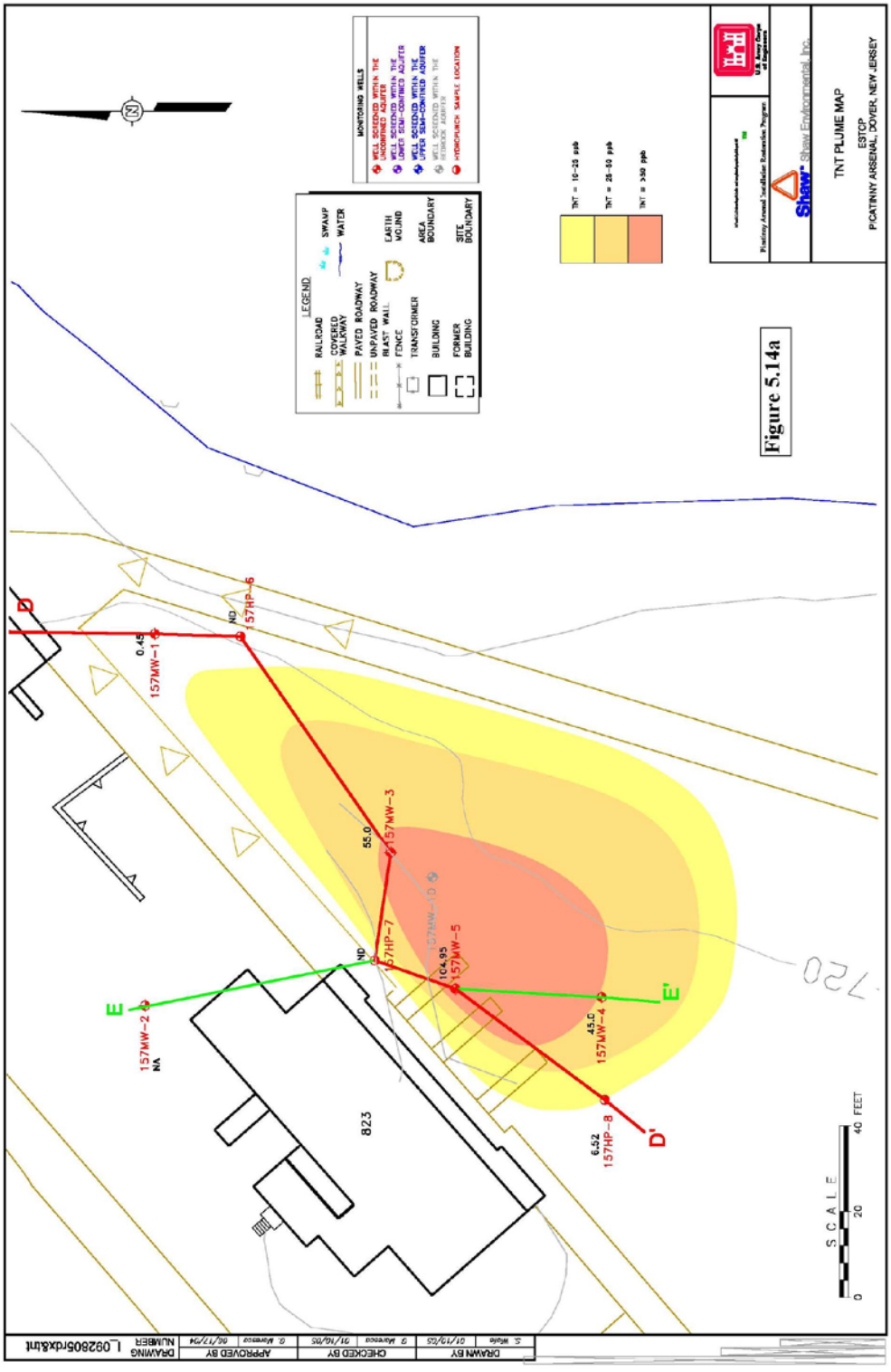


Figure 5.14a. Overhead view of TNT plume in Area 157.

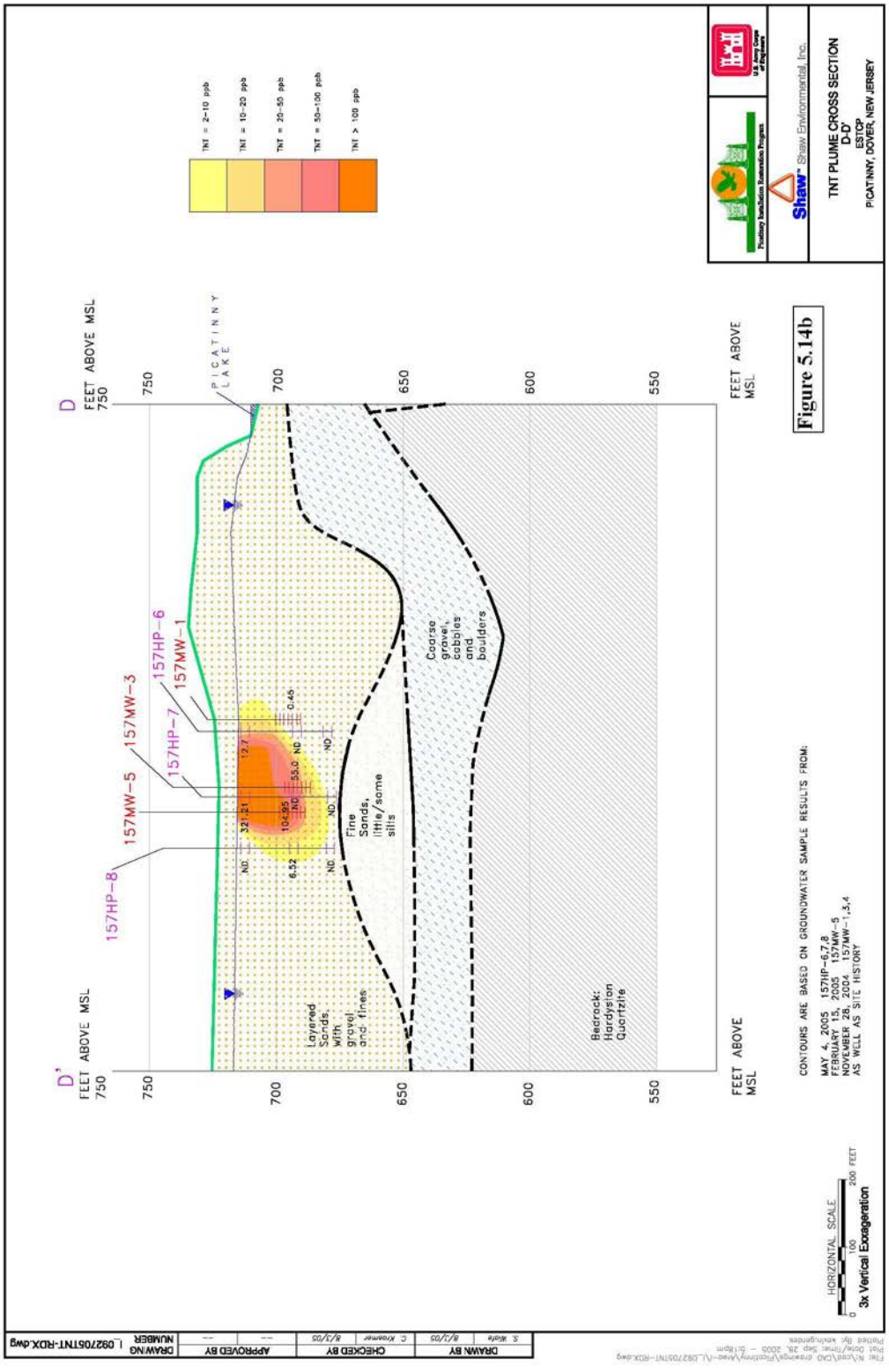


Figure 5.14b. TNT plume cross section D-D'.

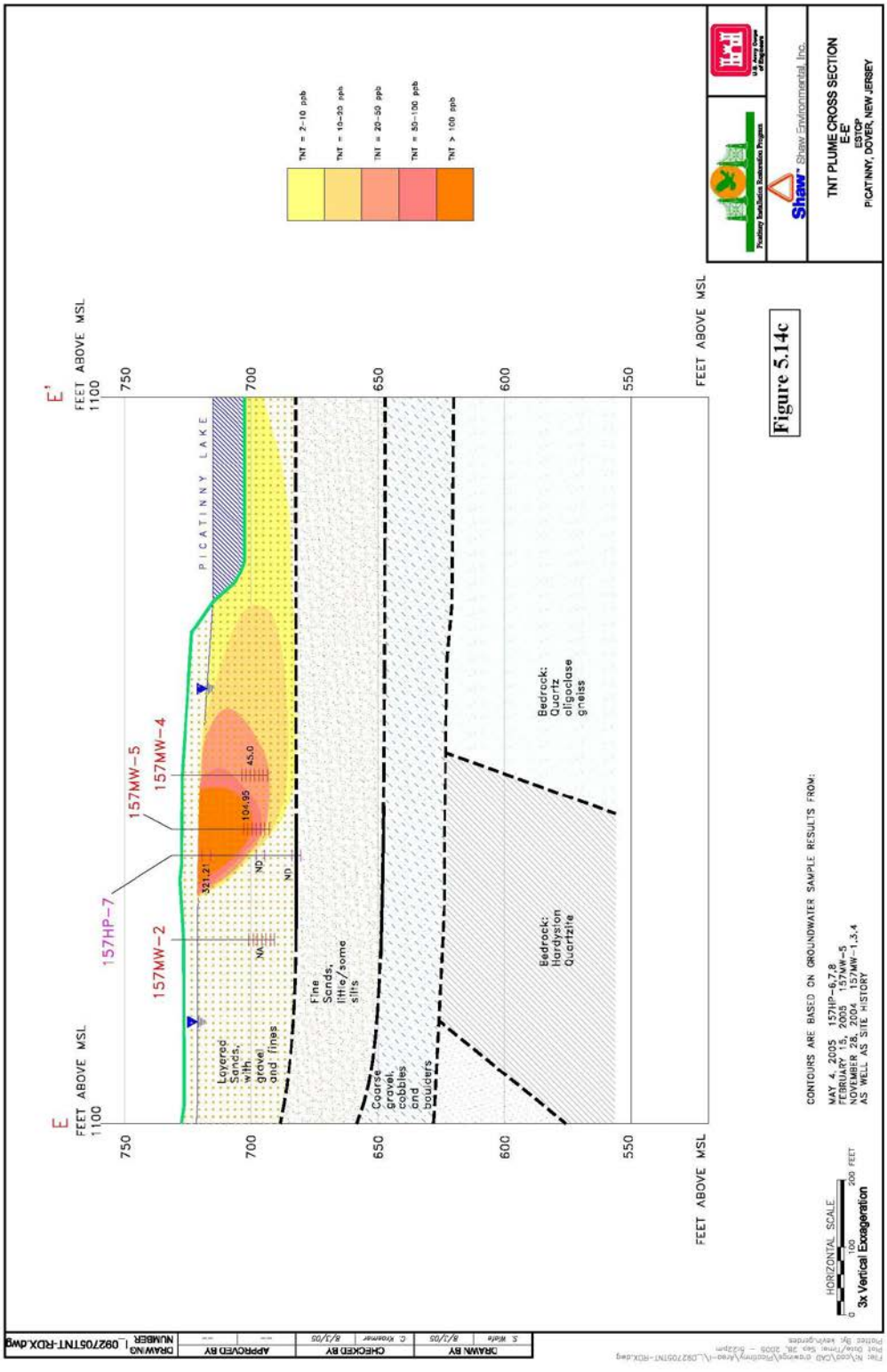


Figure 5.14c. TNT plume cross section E-E'.

5.2.3.2 Supplemental Hydropunch Investigation

Based on the results of the soil and groundwater investigation described in Section 5.2.3.1, as well as recent and historic groundwater monitoring data, a supplemental Hydropunch groundwater investigation was performed in Area 157. The purpose of this supplemental investigation was to verify the vertical extent of groundwater contamination within the treatment zone (thereby defining the vertical extent of the proposed *in situ* bio-treatment system), to confirm the downwards migration of contaminants away from the suspected sources adjacent to Building 823, and to improve delineation on the upgradient and downgradient extent of the dissolved contaminant plume.

Hydropunch samples were collected from four locations, 157HP-9 to 157HP-12, as shown on **Figure 5.15**, using Geoprobe direct-push methods. At each location, groundwater samples were collected ~ every 10 feet starting at the water table (approximately 8 ft bgs) to a maximum depth of ~50 ft bgs. The values for RDX and TNT in these samples are provided in **Table 5.5**.

The data from the supplemental Hydropunch investigation showed shallow groundwater contamination with RDX near the former wastewater discharge lines of Building 823 (157HP-9), which supported previous results. Very little TNT was detected. The investigation also suggested that the groundwater plume was sinking somewhat while moving downgradient (southeast) from Building 823. At the furthest point downgradient (157HP-12), RDX exceeded 5 μg/L from 38 - 52 ft bgs, while the nitramine was near or below detection (< 0.6 μg/L) further upgradient of this point at the same depth. The primary contamination upgradient was from 8-22 ft bgs. As a result of this investigation, the preliminary design of the monitoring well network was modified to include a nested well pair in the vicinity of the 157HP-12 hydropunch (Well pair 157MW-8S/D), with the deeper well screened from 35-50 ft bgs (see Section 5.3.1).

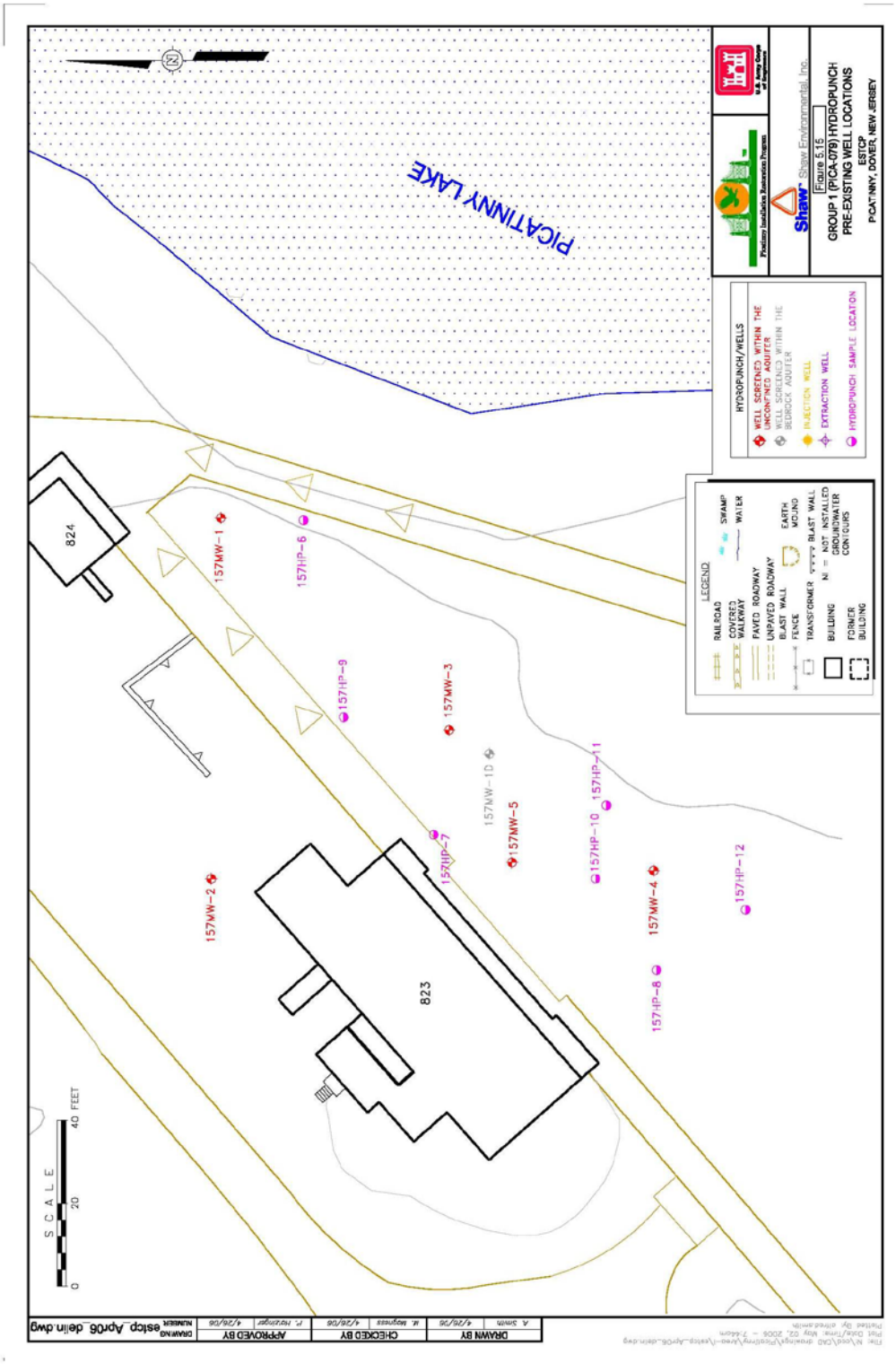


Figure 5.15. Location of original and supplemental Hydropunch samples.

Table 5.5. RDX and TNT Data for Area 157 Supplemental Hydropunch Locations.

Field Sample	Date Sampled	Sample Depth (ft bgs)	Contaminant	
			RDX (ug/L)	TNT (ug/L)
157HP-9A	03/06	8-12	8.86	1.24
157HP-9B	03/06	18-22	3.56	ND
157HP-9C	03/06	28-32	0.2	ND
157HP-9D	03/06	38-42	ND	ND
157HP-9E	03/06	48-52	ND	ND
157HP-10A	03/06	8-12	6.29	ND
157HP-10B	03/06	18-22	28.4	0.17
157HP-10C	03/06	28-32	0.76	ND
157HP-10D	03/06	38-42	ND	ND
157HP-10E	03/06	48-52	ND	ND
157HP-11A	03/06	8-12	9.43	ND
157HP-11B	03/06	18-22	28.3	0.22
157HP-11C	03/06	28-32	2.73	ND
157HP-11D	03/06	38-42	0.5j	ND
157HP-11E	03/06	48-52	0.21j	ND
157HP-12A	03/06	8-12	7.6	ND
157HP-12B	03/06	18-22	14.7	ND
157HP-12C	03/06	28-32	0.42j	ND
157HP-12D	03/06	38-42	12.7	ND
157HP-12E	03/06	48-52	5.81	ND

ND: Non-Detect. The PQLs were 0.6 ug/L and 2 ug/L for RDX and TNT, respectively.
j : Estimated value below the PQL but above the MDL.

5.2.4 Slug Testing

Shaw conducted rising- and falling-head slug tests in April, 2005 on three monitoring wells (157MW-1D, 157MW-4 and 157MW-5) located within Area 157. Wells 157MW-4 and 157MW-5 are screened within the shallow sandy aquifer, while 157MW-1D is screened within the underlying bedrock. Well construction details were summarized previously in Section 5.2.1.

Slug test data were analyzed using the computer software Super Slug™. This software allows the user to analyze the slug test data using the Cooper and/or the Bouwer and Rice methods. Mean hydraulic conductivity values of 2.5 ft/day at 157MW-1D (deep bedrock well), 33 ft/day at 157MW-4, and 18 ft/day at 157MW-5 were calculated. The conductivity values were used in the initial site groundwater model and subsequent treatment system design (Sections 5.2.6 and 5.3).

5.2.5 Pump Testing

Pump testing was performed in Area 157 to:

- Confirm the horizontal hydraulic conductivities measured by the slug testing;
- Determine the aquifer transmissivity and storativity;
- Confirm injection/extraction well flow rates and the hydraulic radius of influence simulated in the conceptual model/system design.

The pump test was centered within the treatment system (**Figure 2.3**). Nested well pair 157MW-6S/D was installed near Hydropunch location 157HP-7 prior to other system monitoring wells in order to facilitate pump testing. The pump test well (157MW-6D) was screened from 30 to 40 ft. bgs, with a 2-inch diameter well screen and a 6-inch borehole. The shallow nested well, designated as 157MW-6S, was screened from approximately 13 to 18 ft. bgs, and constructed similarly to the pump test well.

A step-drawdown pumping test was performed at 157MW-6D on June 14, 2006 to estimate well performance, determine a sustainable optimum pumping rate for a constant rate pumping test, and evaluate aquifer properties. Water was pumped from the test well at 7 gpm, 12 gpm, and 16.5 gpm for ~ 30 min at each rate. The well was then pumped at 17 gpm for ~ 80 min to conclude the step-drawdown test. Drawdown was measured via data loggers in the pumping well and monitoring wells 157MW-1D, 157MW-3, 157MW-5, 157MW-6S, 157MW-7S and 157MW-7D and manually in wells 157MW-1, 157MW-2, 157MW-4, 157MW-8S and 157MW-8D. Results of the testing showed that the pumping well equilibrated relatively quickly at a pumping rate of 17 gpm, without significant drawdown in the pumping well. Results also

showed that a pumping rate of 17 gpm was sufficient to influence all of the shallow monitoring wells within the immediate demonstration area.

Based on these data, a short-term constant rate pumping test was performed on June 15, 2006. Groundwater was extracted at a constant rate of 17 gpm from well 157MW-6D for 6 hrs. The water level drawdown was measured as a function of time in all local monitoring wells as detailed previously. The test was performed until pseudo steady-state conditions were attained (i.e., measured drawdown in test and observation wells constant over time). The recovery of water levels in the pumping well and observation wells was monitored after pumping was terminated. Extracted groundwater was stored on-site in a temporary holding tank (e.g., Baker tank), and then treated through a small carbon vessel (US Filter, Aqua scrub) prior to discharge.

Test data was analyzed using the AQTESOLV aquifer testing software package. Drawdown data as a function of distance from the pumping well were used to determine aquifer hydraulic conductivity, transmissivity, and storativity values of 19.9 ft/day, 1,434 ft^2/day, and 0.066 (dimensionless) respectively. These data are consistent with the slug test data, and consistent with expectations for a sandy, unconfined aquifer. These parameters were used to refine the site groundwater model and verify the final treatment system conceptual design (described in Section 5.3).

5.2.6 Groundwater Modeling and Treatment System Conceptual Design

The system conceptual design was based on results of the laboratory microcosm study, the hydraulic investigations described previously, and a groundwater hydrogeologic fate and transport model. Preliminary system design included the following:

- Location and screen intervals for injection and extraction wells
- Injection/extraction well flow rates
- Location of additional monitoring wells
- Amendment (i.e., cosubstrate, nutrients) selection and dosage

MODFLOW (USGS, 1996), a three-dimensional groundwater flow model, was used to construct a geologic and hydraulic model within the demonstration area. SEAM3D (Waddill and Widdowson, 1998), a solute fate and transport model used within the MODFLOW groundwater flow model, was used to simulate the migration and biodegradation of target contaminants. SEAM3D was also used to evaluate the mixing and fate of cosubstrate amendments and bromide tracer. Both the MODFLOW and SEAM3D models were developed using the site-specific hydraulic, geologic, and biological (i.e., contaminant and cosubstrate biodegradation rates) data obtained during the pre-demonstration testing activities described previously in Sections 5.1 and Sections 5.2.1-5.2.5.

The model was used to facilitate the design of the biotreatment system (i.e. determine treatment well location, pumping rates, and the cosubstrate injection schedule) in order to achieve desired downgradient and source area reductions in TNT, RDX, and HMX groundwater concentrations. The model simulated transport of the cosubstrate and target contaminants in the groundwater flow field induced by operation of the treatment system. Microorganisms were assumed to be immobile, and at a steady concentration throughout the treatment zone. The rate of contaminant degradation was modeled using Monod kinetics, with the cosubstrate present in excess. Kinetic parameters for contaminant biodegradation within the model were estimated based on the laboratory microcosm studies. Additional details of the model are presented in **Appendix C**.

Various conceptual system designs were evaluated using the MODLFOW/SEAM3D fate and transport model. Specifically, the model was used to ensure that the biotreatment system would accomplish the following:

- Completely intercept the contaminant plume in the targeted demonstration zone. Hydraulic capture of the contaminant plume was evaluated by evaluating the radius of influence of the simulated extraction wells in MODFLOW, and by evaluating particle capture;

- Provide sufficient mixing of injected amendments with groundwater. Simulated amendment concentrations in the treatment zone were evaluated as a function of depth and distance from the injection well to determine the well flow rates, spacing, and screen interval needed to ensure proper mixing;

- Biologically degrade TNT and RDX within the treatment zone, thereby preventing downgradient contaminant migration. Simulated contaminant biodegradation rate constants were based on the results of the laboratory microcosm study. These rate constants were used within the model to verify that the conceptual system design provided sufficient residence time such that TNT and RDX concentrations decreased to target levels within the effective influence of the bio-treatment system. The biodegradation of HMX was also evaluated in the model.

- Provide a monitoring well network to sufficiently evaluate system performance. The model was used to determine locations and screen intervals for monitoring wells so that system performance could be assessed. Specifically, wells were placed in locations so that simulated extraction well capture (i.e., drawdown), amendment delivery, and contaminant concentrations could be observed.

The system design based on the MODFLOW/SEAM3D simulation consisted of two extraction wells (EW-1, EW-2) operating periodically (3 days “active”) at 5 gpm each and one injection

well (IW-1) running at 10 gpm. The system was then shut down for 15 days in the "passive" phase. The system utilized the existing monitoring well network, including the new dual-nested well that was installed for the pump test (157MW-6D and 157MW-6S). To adequately monitor system performance, two additional monitoring wells, (157MW-7 and 157MW-8), were included in the initial design. After the preliminary modeling and final Hydropunch data (which showed some depth-dependent differences in explosives concentrations in the treatment area), the original wells 157MW-7 and 157MW-8 were changed from single screened to dual-nested wells and delineated hereafter as 157MW-7S/7D and 157MW-8S/8D. The final well layout is provided in **Figure 5.16**. This change was made to better assess depth-dependent treatment in the aquifer.

The site model was used to simulate TNT and RDX treatment during the demonstration period. **Figure 5.17a** and **Figure 5.17b** show the simulated dissolved TNT concentrations throughout the demonstration area 30 days and 180 days after beginning cosubstrate (cheese whey) injection, respectively. **Figure 5.18a** and **Figure 5.18b** show the simulated dissolved RDX concentrations throughout the demonstration area 30 days and 180 days after beginning cheese whey injection, respectively. **Figure 5.19** shows the simulated steady-state hydraulic head contours during system operation. Also shown in **Figure 5.19** are particle flow paths from presumed upgradient contaminant sources. Simulation results suggest that groundwater across a 115 ft. interval perpendicular to groundwater flow is captured by the treatment system. The assumptions used in development of the model are listed in **Appendix C**. Additional details of the conceptual system design including injection/extraction well flow rates, pulsing frequency, and amendment concentrations and injection rates are also provided in **Appendix C**.

The system described in **Figures 5.16** through **5.19** was expected to generate a zone of reduced contaminant groundwater concentrations that extends 50 ft. wide (perpendicular to groundwater flow), 90 ft. long (parallel to groundwater flow), and within a 25-foot depth interval below the water table. Based on the model simulations, the locations of monitoring wells allow for verification of hydraulic control and amendment distribution, as well as evaluation of contaminant biodegradation within the treatment zone. Monitoring well 157MW-8 serves as a far downgradient monitoring point (modified to a MW pair 157MW-8S/8D), and monitoring wells 157MW-1 and 157MW-2 serve as upgradient monitoring points. Based on the model simulations, it is anticipated that TNT and RDX emanating from upgradient of the biotreatment system will attain the target groundwater criteria (2 μg/L) before migrating downgradient towards the 157MW-8S/D location.

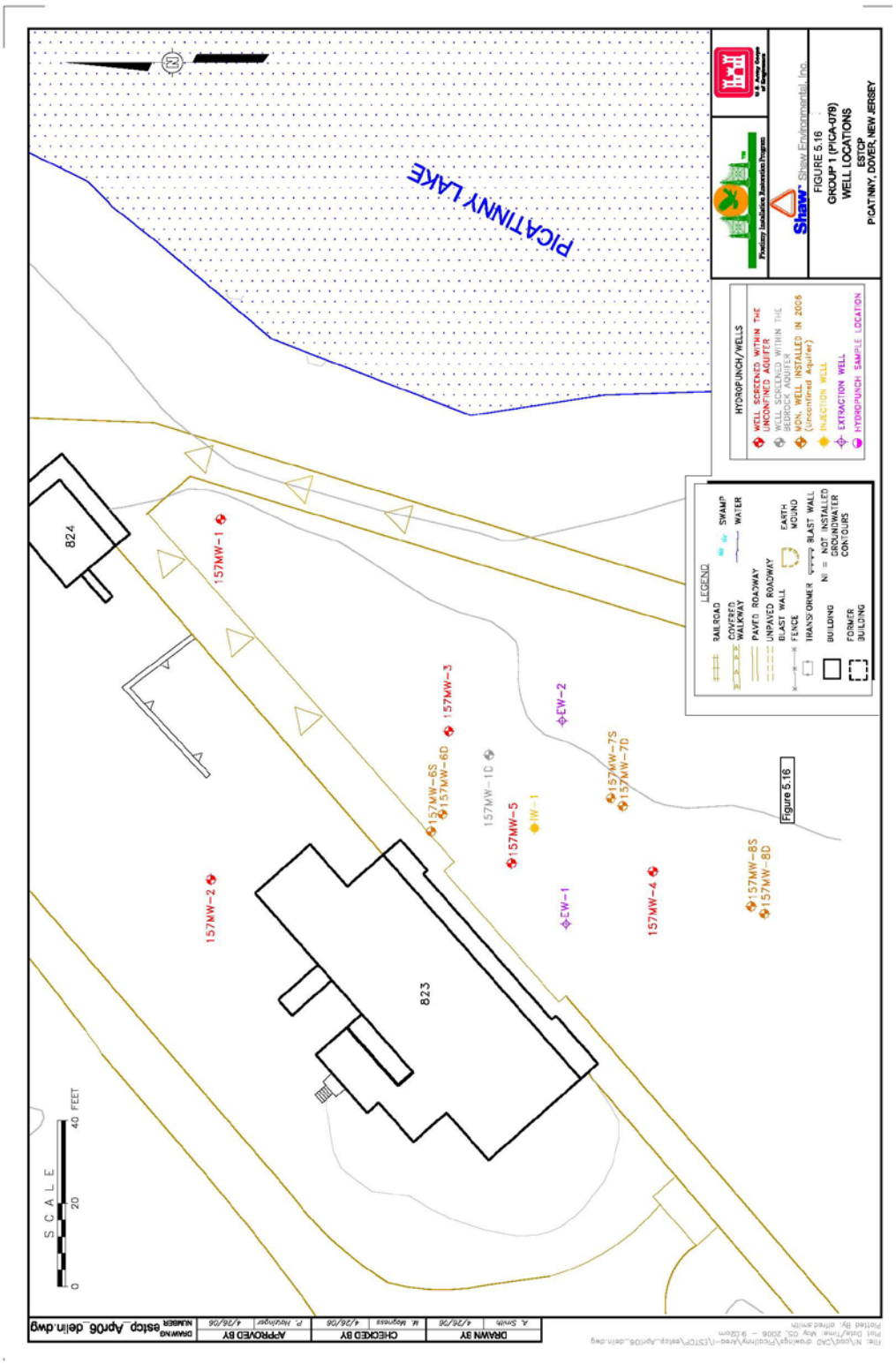


Figure 5.16. Test plot design.

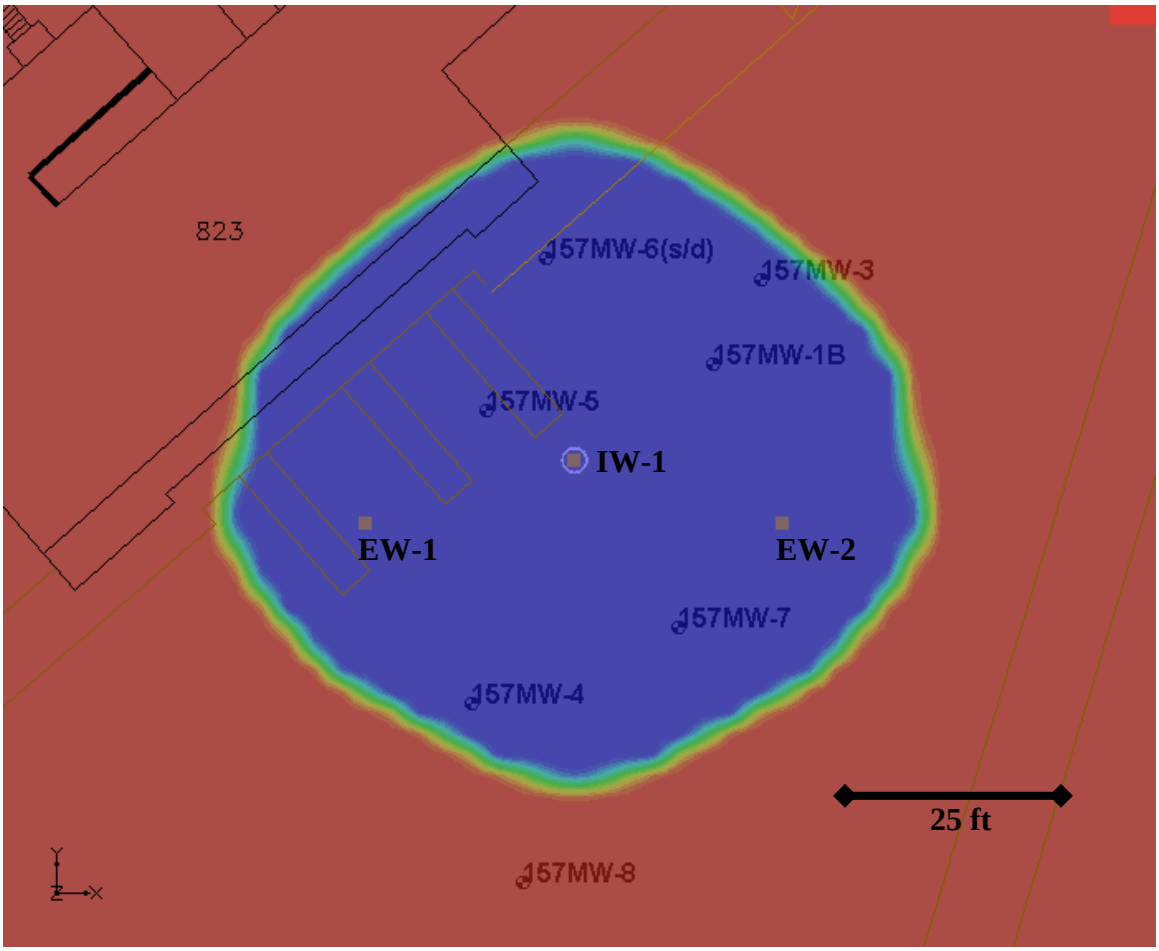


Figure 5.17a. Simulated TNT groundwater concentrations at T=30 days of system operation. Shading (blue to red) represents TNT groundwater concentrations ranging from <1 µg/L to 40 µg/L, respectively. Square symbols represent simulated extraction wells (5 gpm each), and the encircled square symbol represents the simulated injection well (10 gpm).

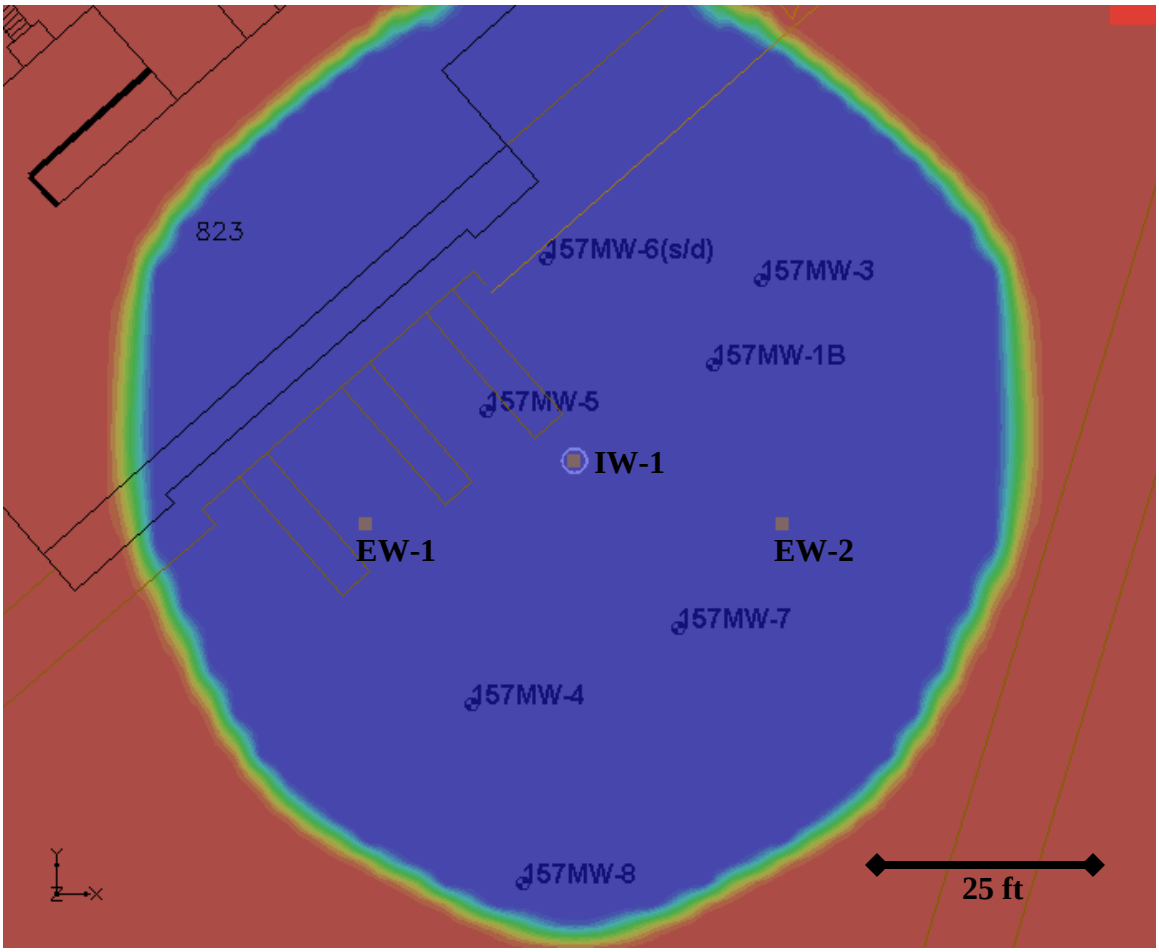


Figure 5.17b. Simulated TNT groundwater concentrations at T=180 days of system operation. Shading (blue to red) represents TNT groundwater concentrations ranging from <1 µg/L to 40 µg/L, respectively. Square symbols represent simulated extraction wells (5 gpm each), and the encircled square symbol represents the simulated injection well (10 gpm).

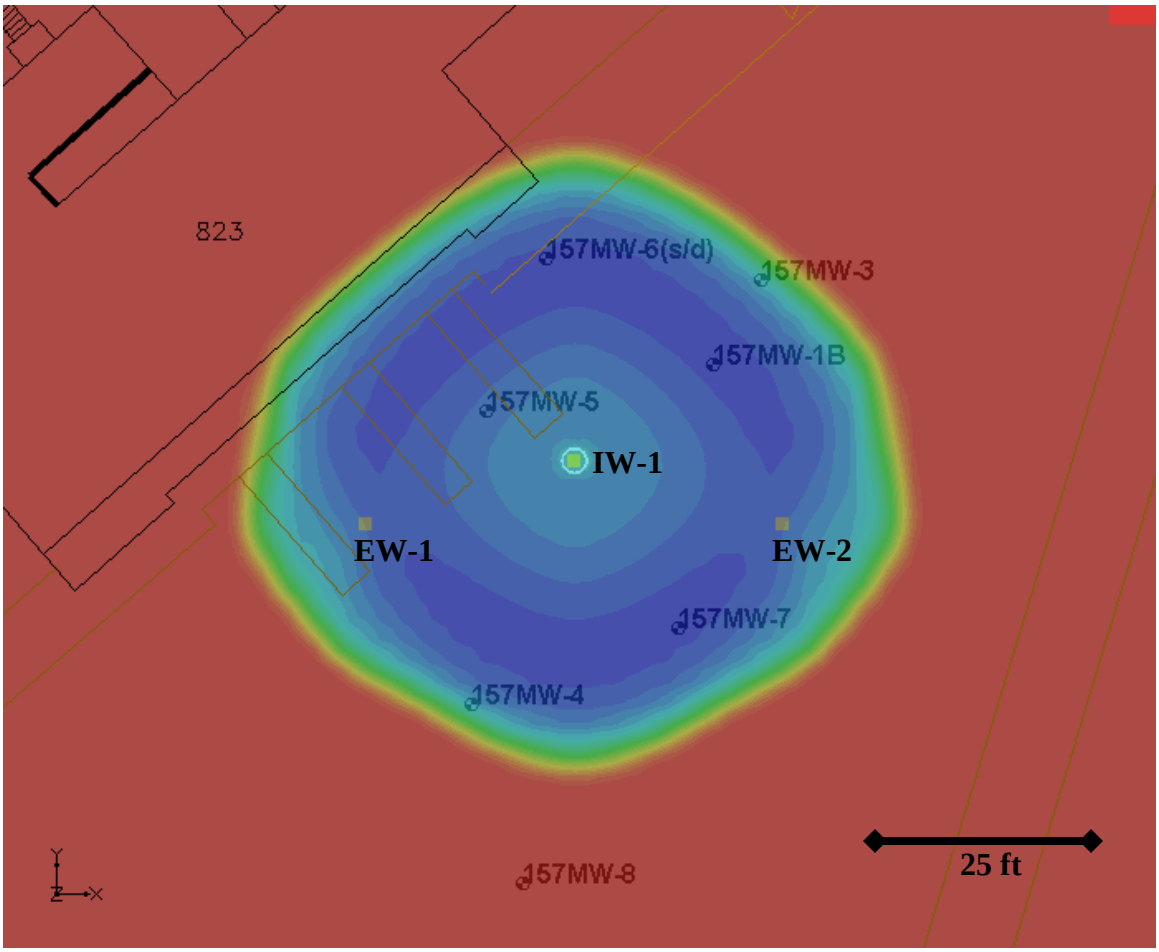


Figure 5.18a. Simulated RDX groundwater concentrations at T=30 days of system operation. Shading (blue to red) represents RDX groundwater concentrations ranging from <1 µg/L to 70 µg/L, respectively. Square symbols represent simulated extraction wells (5 gpm each), and the encircled square symbol represents the simulated injection well (10 gpm).

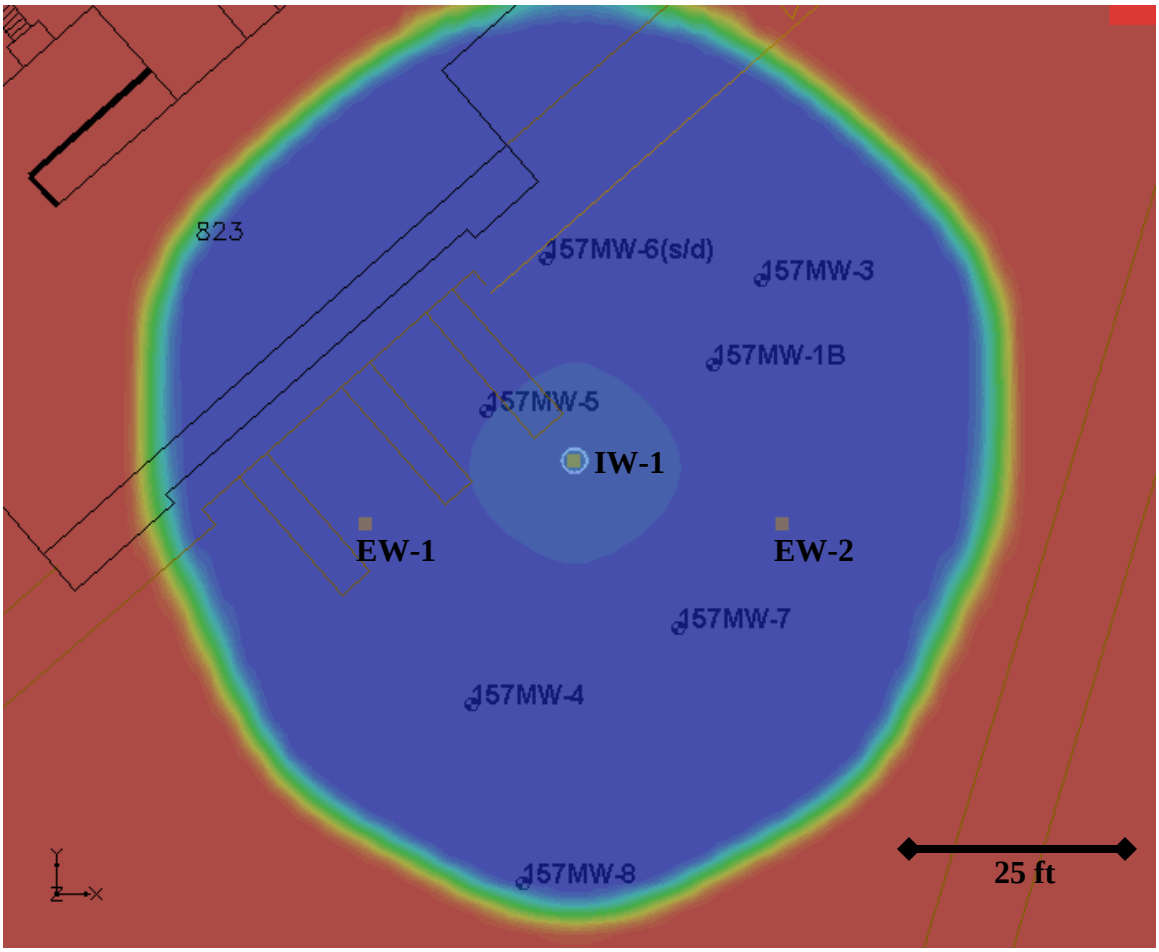


Figure 5.18b. Simulated RDX groundwater concentrations at T=180 days of system operation. Shading (blue to red) represents RDX groundwater concentrations ranging from <1 µg/L to 70 µg/L, respectively. Square symbols represent simulated extraction wells (5 gpm each), and the encircled square symbol represents the simulated injection well (10 gpm).

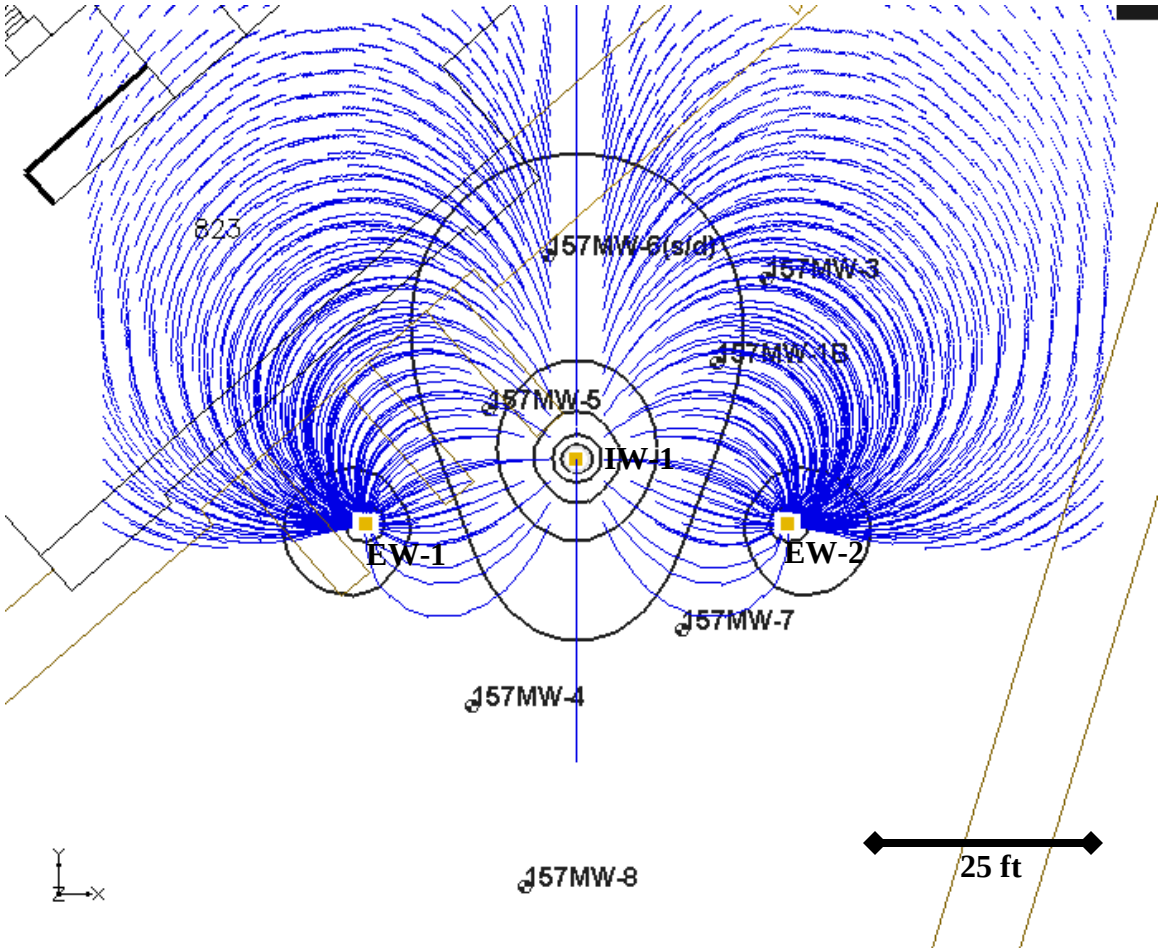


Figure 5.19. Simulated hydraulic head contours (black lines) and particles flow paths (blue lines). Simulated contours range from -0.8 ft of relative head (adjacent to extraction wells) to +1.0 ft of relative head (adjacent to injection well).

5.3 Design and Layout of Technology Components

The main technology components for this demonstration included (1) injection, extraction, and monitoring wells, (2) a cosubstrate injection system, and (3) a control system to regulate groundwater extraction and recharge as well as cosubstrate addition. The design, layout and installation of these technology components are detailed below.

5.3.1 Well Installations

The final well layout for the demonstration system is provided in **Figure 5.16**. The final four monitoring wells (157MW-7S/D; 157MW8-S/D) were installed using the drilling methods described in Section 5.2.1. In summary, the wells were installed using a hollow stem auger (HAS) drill rig, with a 4.25-inch drill bit. The depths and screened intervals of thee wells are provided in **Table 5.6** and the locations in **Figure 5.16**. The monitoring wells were constructed with 2-inch inner diameter, flush threaded, Schedule 40 PVC casing and factory slotted (0.010-inch) screen, with screen intervals of 10 ft for 157MW-7S/D and 15 ft for 157MW-8S/D. Downgradient well 157MW-8D was screened deeper (35 – 50 ft bgs) than any of the other monitoring wells based on Hydropunch data suggesting that the plume was dipping slightly as it moved downgradient. Clean silica sand (#1 size) was used in the filter pack around the well screens, extending from the bottom of the well screen to five feet above the top of the screen. A 3-ft bentonite seal was installed above each well screen. The remaining annulus for each well was sealed with a cement/bentonite grout mixture and finished with a 2 ft stick-up set in a concrete pad level with the surrounding terrain.

The bio-treatment system employed a pair of extraction wells (EW-1 and EW-2) and a single injection well (IW-1) to mix co-substrate with the contaminated groundwater. The wells were placed cross-gradient to the prevailing groundwater flow direction (southeast) as shown in **Figure 5.16**. The extraction wells were placed approximately 50 ft apart with the injection well centered between the two EWs and ~ 7.5 ft upgradient. The injection and extraction wells were also installed using an HSA rig as described previously. Each well consisted of flush-threaded, 4-inch diameter, schedule 80, PVC in an 8-inch diameter borehole. Each extraction well was equipped with 25 feet of 0.020-inch slotted screen extending from approximately 9 to 34 ft bgs (~ 711 to 686 feet MSL). The injection well was installed with a slightly shorter slotted screen interval (~11- 34 ft bgs) to allow enough space and blank casing for a packer to be installed above the screen. The packer was included to allow injection of groundwater into the well under moderate pressure if biofouling occurred.

The filter pack for each extraction/recovery well consisted of silica sand extending ~ 2 feet above the top of screen. A 1 foot transition pack of #30 sand was placed above the silica sand. A seal of bentonite chips was placed above the filter pack as described previously. The remaining annular space was filled with cement-bentonite grout. Each extraction well was completed with a stickup installed in a 36-inch by 36-inch concrete pad at the ground surface. Approximately 2 ft of PVC was left above the top of the stick-up monument after installation so that extraction

equipment could be installed (pitless adaptor, water lines, etc). The injection well was installed in a flush-mounted monument, but the PVC was left ~ 3 ft above the top of the monument for installation of necessary equipment.

After installation, each monitoring or injection/extraction was developed via surging and pumping with a submersible pump. Investigation derived waste (IDW), including equipment decontamination rinseate and waste soil, was managed in accordance with Picatinny Arsenal guidelines. Field activities were completed in Level D Protection. Procurement of permits, utility clearance, unexploded ordnance and explosive waste clearance, and well surveying were also conducted in accordance with Picatinny Arsenal guidelines.

5.3.2 Well Pump, Piping, and Controls Installation

A pumping and instrumentation diagram (P&ID) showing the general design of the extraction and injection wells and the associated equipment is provided in **Figure 5.20**. Submersible variable-speed pumps (Well Pump P100 & P200; Grunfos, Redi-Flo3) were used in the extraction wells (EW -1 and EW-2) to remove groundwater from the aquifer. Each of the EW pumps was set 5 ft from the bottom of the screen interval of the EW. Piping was run from each pump to a pitless adaptor placed in the PVC casing of each extraction well. Tubing was then connected to that adaptor and run from each extraction pump through conduit to a Conex box, which was centrally located in the demonstration area near the Injection Well (IW-1). The Conex box contained the control panel, computer, filter units, flow meters, and 3-phase/240V/200 Amp power service as reflected in the system process P&ID. It also served as a secure location to store compressors and other materials required for well sampling and basic system O&M. Electrical conduits were run from the main power supply to the Conex box and extraction wells. Photographs of EW-1, the demonstration plot, and the Conex box are provided in **Figures 5.21-5.23**.

Within the Conex box, the tubing from each extraction well was run through a filter unit (F100 & F200) to remove any solids and then through individual flow meters. The flow from each of the extraction wells was then combined and piped to the injection well (IW). A dosing pump (P-600) was used to add the dissolved cheese whey to the combined flow from the EWs during active treatment phases. The water was filtered after cheese whey addition to remove any solids. More details on the cosubstrate dissolution and injection system are provided below. The injection well was fitted with a submersible pump (P-200; Grunfos Redi-Flo-3) that was used to enhance the mixing of the cheese whey with the water in the injection well. In addition, the injection well was fitted with a custom packer near the surface of the water table to allow injection of water under moderate pressure. Pressure transducers were installed in each extraction and the injection well to evaluate pressure drop and determine if biofouling was occurring. Valves, gages, and fittings were installed as necessary to complete the piping runs and connections as detailed in the system process P&ID (**Figure 5.20**).

Cheese whey was purchased from International Ingredient Co. in St. Louis, MO in 50 lb (23 kg) bags. A total of 2,000 lbs (870 kg) was purchased for the demonstration. The whey product used is routinely packaged as an animal feed additive. The same whey was used in the laboratory microcosm and column studies. The basic specifications for the whey are provided in **Figure 5.24.** A 1400-gal (5300 L) conical bottom tank was designed to allow mixing of the powdered cheese whey with water **(Figure 5.25)**. To enhance mixing, a series of spray nozzles were installed in the upper portion of the tank. A jet pump was attached to a port at the bottom of the tank through flexible tubing. The whey solution in the tank was initially recirculated from the bottom of the tank through the pump and discharged through the spray nozzles at the upper portion of the tank for 1-2 hrs. This allowed thorough mixing and solubilization of the whey. Once in solution, they whey tank was connected to the dosing pump in the Conex box, and the solution could then be added to the IW. Any insoluble material which settled in the tank was removed through an access port after all soluble material was added to the aquifer. Details concerning the quantities of whey added are provided in Section 5.4.

Table 5.6. As-Built Well Details.

Well I.D.	Well Diameter (inches)	Screened Interval (ft bgs)	Total Depth (msl)	Land Elev. (msl)	TIC Elev. (msl)	Aquifer
157MW-1D	4	134-144	573.66	717.5	719.73	Bedrock - Hardyston Quartzite
157MW-2	4	23.6-33.6	684.66	716.99	720.10	Unconsolidated
157MW-3	4	23.4-33.4	684.62	717.86	720.75	Unconsolidated
157MW-4	2	24-34	683.3	717.29	719.55	Unconsolidated
157MW-5	2	24.5-34.5	NS	718.3	717.80	Unconsolidated
157MW-6S	2	13-18	699.51	717.51	718.69	Unconsolidated
157MW-6D	4	30-40	677.60	717.60	719.92	Unconsolidated
157MW-7S	2	10-20	697.62	717.62	719.85	Unconsolidated
157MW-7D	2	25-35	682.58	717.58	719.67	Unconsolidated
157MW-8S	2	15-30	686.23	716.23	718.63	Unconsolidated
157MW-8D	2	35-50	666.20	716.20	718.63	Unconsolidated
EW-1	4	9-34	682.84	716.84	721.01	Unconsolidated
EW-2	4	9-34	684.96	718.96	721.46	Unconsolidated
IW-1	4	11-34	683.40	717.40	721.67	Unconsolidated

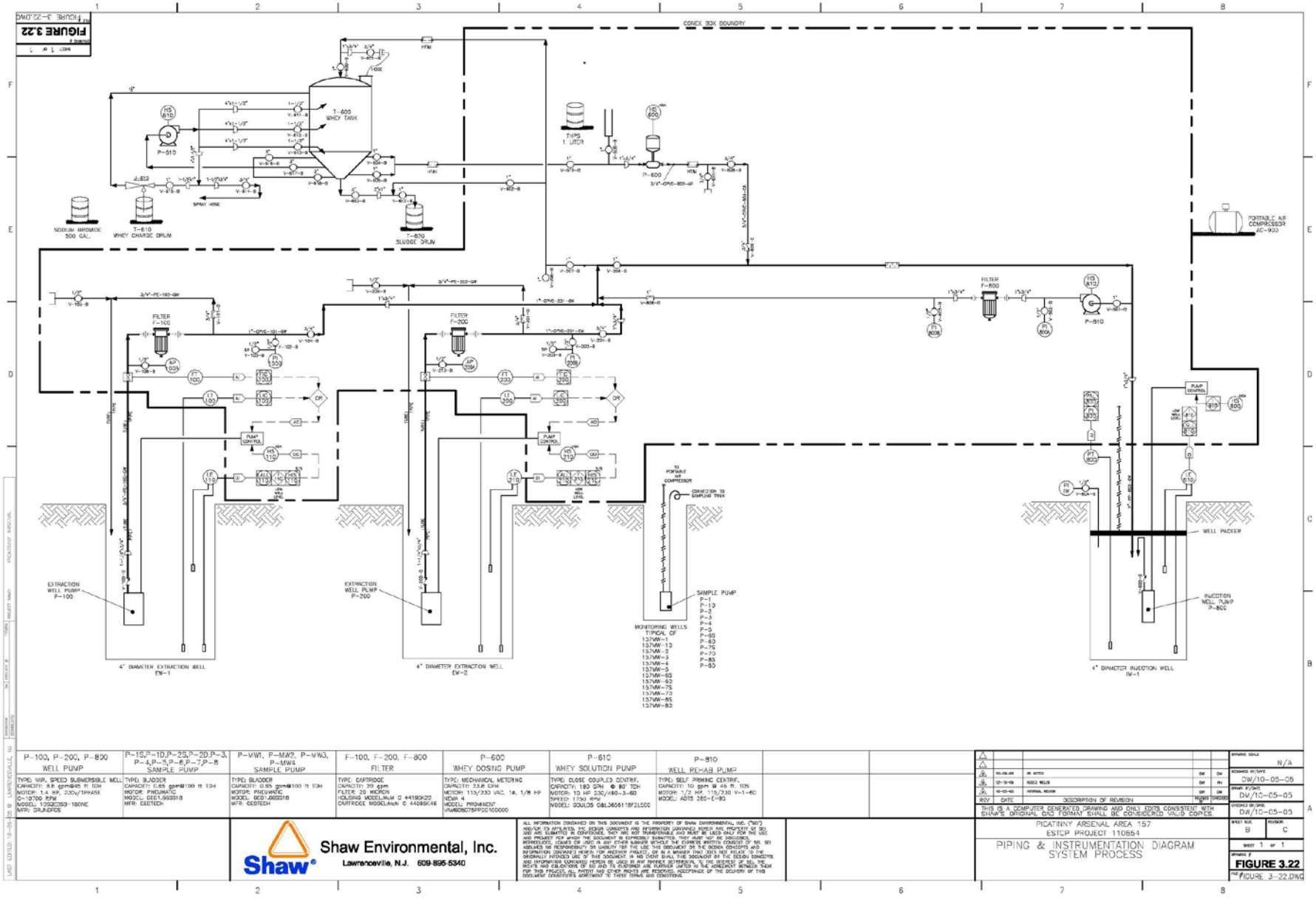


Figure 5.20. Piping and Instrumentation diagram (P&ID) for the Picatinny extraction-reinjection system.

Figure 5.21. Photograph of EW-1.

Figure 5.22. Photograph of demonstration plot with Conex box, IW-1, EW-1 and EW-2 denoted.

Figure 5.23. View inside the Conex box

INTERNATIONAL INGREDIENT CORPORATION
4240 Utah Street • Box 22106 • St. Louis, MO, USA 63116 • (314) 776-2700 • Fax (314) 776-3395

SPECIFICATION SHEET

PRODUCT: Cheese Whey (50:50)

PRODUCT DESCRIPTION: An animal feed ingredient comprised of Cheese Plus Cheese Product and Spray Dried Whey.

TYPICAL ANALYSIS:

Crude Protein	22.75%
Crude Fat	10.5%
Crude Fiber	0.5%
Ash	7.0%
Moisture	5.50%
Salt	3.0%
M.E. (calculated)	1,820 kcal/lb

Amino Acids:

Arginine	0.82%	Cystine	0.39%
Histidine	0.57%	Phenylalanine	1.06%
Isoleucine	1.09%	Tyrosine	0.51%
Leucine	2.61%	Threonine	1.12%
Lysine	1.97%	Tryptophan	0.28%
Methionine	0.58%	Valine	1.18%

Minerals:

Calcium	0.58%	Phosphorus	0.64%
Magnesium	0.11%	Potassium	1.16%

COLOR: Light orange.

TEXTURE: Granular powder.

PACKAGING: Bulk truckloads, totes or 50-lb multi-walled bags.

STORAGE: Store in cool dry place.

Figure 5.24. Specifications for cheese whey.

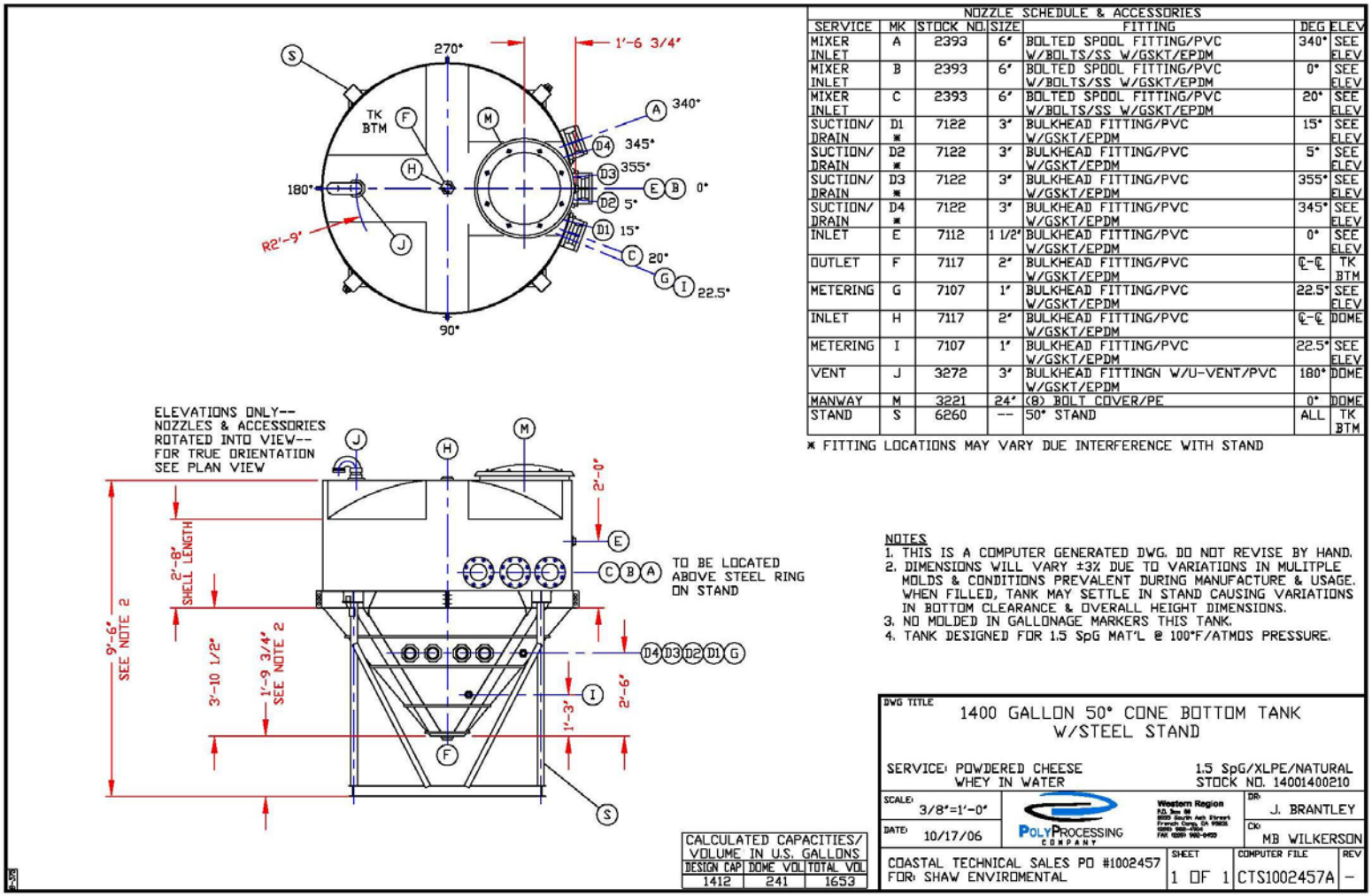


Figure 5.25. Conical bottom tank used to mix and distribute cheese whey.

5.3.3 Biofouling Mitigation Approach

As described in Section 2.4, microbial biofouling is a significant concern with any *in situ* remedial system, and particularly with those requiring active pumping. Various chemical and operational approaches have been tested to mitigate biofouling, including "oxidizing" amendments (e.g., chlorine dioxide, sodium hypochlorite, and hydrogen peroxide), acid treatment, enzyme addition, liquid carbon dioxide, intermittent pumping strategies, and other techniques. At present, there does not appear to be a "magic bullet" for this problem. Rather, a combination of strategies may prove to be most effective. During this demonstration, several techniques to control biofouling were utilized, including: (1) pumping groundwater intermittently rather than continuously and injecting high doses of cheese whey during the intermittent pumping; (2) injecting groundwater through a pressurized packer to promote movement of water into the formation; and (3) treating the injection well with Tetrakis(hydroxymethyl)phosphonium sulfate (THPS), a biodegradable anti-fouling agent, if necessary based on increased injection well pressure during active operation. THPS is a non-toxic microbial biocide that was developed in the mid-1990s (Frey, 1998). After a three-year review process, the USEPA permitted registration of the compound, and it was awarded the "Green Chemistry Award" by USEPA in 1997 (USEPA, 2005). The advantages of this compound for biofouling control include effectiveness at a low dose, low human and environmental toxicity, and rapid environmental breakdown to non-toxic products through hydrolysis, oxidation, photodegradation, and biodegradation (Frey, 1998; USEPA, 2005).

5.4 Field Testing

5.4.1 Baseline Monitoring

Two groundwater sampling events were performed prior to injection of the cosubstrate (cheese whey) or operation of the groundwater recirculation system in order to provide a baseline with which to compare sampling results both during and following completion of the project. Two additional events were conducted after start-up of the recirculation system but prior to amendment with cheese whey as a cosubstrate. The latter two events are detailed in Section 5.4.2. Groundwater sampling was conducted using dedicated bladder pumps installed in each of the site's 12 monitoring wells (157MW-1, 157MW-1D, 157MW-2, 157MW-3, 157MW-4, 157MW-5, 157MW-6S, 157MW-6D, 157MW-7S, 157MW-7D, 157MW-8S, and 157MW-8D). All site monitoring wells were sampled in each of the two events with the exception of 157MW-1 during Baseline Sampling Event #2. Additionally, samples were collected from the two extraction wells (EW-1 and EW-2) during the second event utilizing the system extraction wells and sampling ports installed on system piping. Analyses performed for each sampling event are summarized below and in **Table 5.7.**

- Baseline Sampling Event #1 – January 17 & 18, 2007 (Day -131 & -130)
    - Baseline explosives plus degradation products
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)

    - Metals (iron and manganese)
    - Total Organic Carbon (TOC)

- Baseline Sampling Event #2 – March 15, 2007 (Day -76)
    - Baseline explosives plus degradation products
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)
    - TOC

5.4.2 Bromide Tracer Test

Prior to injecting cheese whey, a tracer test was performed to evaluate/verify local hydrogeological characteristics and to accurately determine the extent of the capture zone and radius of influence of each extraction well in the treatment system. The tracer test consisted of amending 4,100 liters (L) of site groundwater with 12.5 kilograms (kg) of sodium bromide as a conservative tracer. Bromide amended groundwater was metered into the recirculated groundwater at a rate of approximately 57 liters-per-hour (LPH) over a period of three days. All site MWs and EWs were sampled on a weekly basis following bromide injection and recirculation system operation with the exception of the two EWs during Bromide Tracer Sampling Event #3. During the April 18, 2007 sampling event the recirculation system was discovered non-operational due to an error in the Process Logic Control circuitry, which required a reset by the vendor. It is believed that the error was caused by a power failure during an electrical storm during the previous week. Bromide was analyzed in all samples by EPA Method 300.0 (ion chromatography). Other anions in groundwater, including nitrate, nitrite, sulfate, and chloride were also analyzed during the initial sampling events in order to provide a broader baseline picture of the aquifer geochemistry. Results from the baseline sampling events showed that the background concentrations of bromide were negligible. In addition, samples from Bromide Tracer Sampling Events #3 and #4 were analyzed for baseline explosives and daughter products of TNT and RDX, in order to evaluate changes in their groundwater concentrations due to the operation of the recirculation system. Thus, four sampling events were conducted prior to cheese whey addition – two prior to groundwater recirculation and two after substantial recirculation of groundwater. Key events associated with the bromide tracer test are summarized below:

- Bromide Tracer Injection – March 27-30, 2007 (Days – 66 to -64)
    - 12.5 kg of sodium bromide in solution with 4,100 L of site groundwater
- Bromide Tracer Sampling Event #1 – April 3, 2007 (Day -61)
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)
- Bromide Tracer Sampling Event #2 – April 10, 2007 (Day -57)
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)
- Bromide Tracer Sampling Event #3 & Baseline Event # 3 – April 18, 2007 (Day -42)
    - Baseline explosives plus degradation products
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)

- Bromide Tracer Sampling Event #4 & Baseline Event # 4 – May 3, 2007 (Day -27)
    - Baseline explosives plus degradation products
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)
    -

5.4.3 Performance Monitoring

System operation consisting of groundwater recirculation in conjunction with the injection of cheese whey commenced on May 30, 2007 (Day 0). Site groundwater amended with powdered cheese whey was initially metered at a flow rate of approximately 57 LPH. The actual injection rate varied somewhat due to periodic clogging of the cartridge filter installed on the outlet of the whey tank. Regular filter changes and adjustments to the metering pump frequency and stroke were made in order to maintain the desired metering flow rate. Samples were collected from the treatment zone monitoring wells (TMZWs; 157MW-5, 157MW-6S, 157MW-6D, 157MW-7S, and 157MW-7D) and analyzed for TOC as a measure of cheese whey distribution. For the remaining sampling events, samples were collected from all site MWs and EWs and analyzed for the complete suite of analytical parameters. Key events of the system operation and performance monitoring conducted to date are summarized below:

- Cheese Whey Injection Event #1 – May 30-June 1, 2007 (Day 0-Day 3)
    - 4,100 L of site groundwater was amended with 230 kg of powdered cheese whey

- Performance Monitoring Sampling Event #1 – June 14, 2007 (Day 14)
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)
    - TOC

- Performance Monitoring Sampling Event #2 – July 2, 2007 (Day 33)
    - Baseline explosives plus degradation products
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)
    - Metals (iron and manganese)
    - TOC

- Cheese Whey Injection Event #2 – July 10-13, 2007 (Day 41-44)
    - 2300 L of site groundwater was amended with 140 kg of powdered cheese whey

- Performance Monitoring Sampling Event #3 – July 31, 2007 (Day 62)
    - Baseline explosives plus degradation products
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)
    - TOC

- Performance Monitoring Sampling Event #4 – September 05, 2007 (Day 98)
    - Baseline explosives plus degradation products
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)
    - TOC

- Cheese Whey Injection Event #3 – September 10-13, 2007 (Day 103-107)
    - 4,100 L of site groundwater was amended with 230 kg of powdered cheese whey

- Performance Monitoring Sampling Event #5 – October 25, 2007 (Day 148)
    - Baseline explosives plus degradation products
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)
    - TOC
    - Methane, ethane, ethene in select wells

- Cheese Whey Injection Event #4 – November 27 – November 30, 2007 (Final Addition; Day 181-185)
    - Additional mixing without injection from December 03-06, 2007
    - 4,100 L of site groundwater was amended with 230 kg of powdered cheese whey

- Performance Monitoring Sampling Event #6 – January 07, 2008 (Day 222)
    - Baseline explosives plus degradation products
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)
    - TOC
    - Methane, ethane, ethene in select wells

- Performance Monitoring Sampling Event #7 – February 28, 2008 (Day 274)
    - Baseline explosives plus degradation products
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)
    - TOC
    - Methane, ethane, ethene in select wells

5.4.4 Rebound Monitoring

Two groundwater sampling events were performed to assess longevity of injected cheese whey and rebound of explosives. These events were performed ~ 5 months and 8 months after the final cheese whey injection. A third sampling event was conducted to collect samples for SERDP Project ER-1607 approximately 12.5 months after the final cheese whey injection. Eight of the site monitoring wells were sampled during this event. These data are included herein as a third rebound event. The rebound events were as follows:

- Rebound Sampling Event #1 – May 07, 2008 (Day 343)
    - Baseline explosives plus degradation products
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate)
    - Metals (iron and manganese)
    - TOC
    - Methane, ethane, ethene in select wells

- Rebound Sampling Event #2 – July 23, 2008 (Day 420)
    - Baseline explosives plus degradation products
    - Anions (chloride, nitrate, nitrite, sulfate, bromide, phosphate, and chlorate)
    - TOC
    - Methane, ethane, ethene in select wells
    - Metals (iron and manganese) in select wells
    -
- Rebound Sampling Event #3– December 15, 2008 (Day 565: Wells 157MW-1, 157MW-2, 157MW-4, 157MW-5, 157MW-6D, 157MW-7S, 157MW-7D, and 157MW-8D)
    - Baseline explosives plus degradation products
    - Anions (nitrate, nitrite, sulfate, bromide, phosphate)
    - Metals (iron and manganese)

5.4.5 System Decommissioning

At the conclusion of the demonstration, the system was decommissioned. The groundwater sampling pumps and Grunfos pumps were removed from each well, cleaned, and stored for potential future use on DoD projects. All piping and electrical wire on the ground surface was removed and discarded. Each well was sealed with an appropriate cover and left in place. The electrical supply to the Conex box was unhooked by a qualified electrician. Reusable materials within the Conex box including the system computer, metering pumps, flow meters, compressor, and filter housings were cleaned and placed in storage. The Conex box and the cheese whey tank and tank stand were transported to a Shaw storage facility in West Windsor, NJ for potential future use. At the conclusion of decommissioning, the site was clean of any remining equipment or debris from the ESTCP demonstration.

Table 5.7. Sampling and Operational Schedule.

Starting Date	Activity	Day of Operation
Baseline Monitoring (before recirculation)		
1/17/2007	Baseline Sampling Event #1	Day -131
3/15/2007	Baseline Sampling Event #2	Day -76
System Start-Up		
3/27/2007	Systems Testing & Start-Up	Day -66
Bromide Tracer Testing & Baseline Monitoring (after recirculation)		
3/27/2007	Bromide Tracer Injection and Recirculation	Day -66
4/3/2007	Bromide Sampling Event #1	Day -61
4/10/2007	Bromide Sampling Event #2	Day -57
4/18/2007	Bromide Sampling Event #3 & Baseline Sampling Event #3	Day -42
5/3/2007	Bromide Sampling Event #4 & Baseline Sampling Event #4	Day -27
Operation & Performance Monitoring		
5/30/2007	First Cosubstrate Injection (3 days recirculation)	Day 0
6/14/2007	Performance Sampling Event #1 (TOC and anions only)	Day 14
7/2/2007	Performance Sampling Event #2	Day 33
7/10/2007	Second Cosubstrate Injection (4 days recirculation)	Day 41
7/31/2007	Performance Sampling Event #3	Day 62
9/5/2007	Performance Sampling Event #4	Day 98
9/10/2007	Third Cosubstrate Injection (4 days recirculation)	Day 103
10/25/2007	Performance Sampling Event #5	Day 148
11/27/2007	Fourth Cosubstrate Injection (4 days recirculation)	Day 181
12/3/2007	Additional recirculation without injection (4 days)	Day 188
1/7/2008	Performance Sampling Event #6	Day 222
2/28/2008	Performance Sampling Event #7	Day 274
Rebound Evaluation		
5/7/2008	Rebound Sampling Event #1	Day 343
7/23/2008	Rebound Sampling Event #2	Day 420
12/15/2008	Rebound Sampling Event #3 (subset of wells)	Day 565
Decommisioning		

5.5 Sampling Methods

5.5.1 Groundwater Sample Collection

Groundwater samples were collected during the demonstration based upon USEPA Region 9's "Standard Operating Procedure for Low Stress (Low Flow) / Minimal Draw-down Ground-Water Sample Collection" (http://www.epa.gov/region9/qa/pdfs/finalsopls1217.pdf). Samples were obtained from each well using dedicated submersible bladder pumps with Teflon bladders and tubing. A flow-through cell with connected to a YSI 600XL field meter (YSI, Inc., Yellow Springs, OH) or equivalent was utilized to measure field geochemical parameters (pH, ORP, temperature, specific conductivity, and dissolved oxygen). Sampling was conducted only after field parameters were stable based on low-flow sampling guidelines, and exceptions were noted on field sheets when they occurred. An example of a completed field sheet for low-flow sampling is provided as **Figure 5.26**. All field meters were calibrated according to manufacturer guidelines once at the beginning of the day and calibration was checked if any sampling parameters were outside of the anticipated range. The submersible bladder pumps used to sample all wells were dedicated and therefore decontamination between wells was not required.

Groundwater elevation measurements were collected using an electronic water level indicator prior to collecting groundwater samples and every 5 minutes during low-flow sampling. Measurements were obtained from the top-of-casing and recorded to the nearest 0.01-foot. Groundwater elevation data were used to establish baseline water table elevations, and hydraulic gradient and groundwater flow directions within the Demonstration Area as well as to ensure that excessive drawdown did not occur during low-flow sampling.

Groundwater samples were collected from the demonstration monitoring wells and extraction wells listed in **Table 5.6** (excluding IW-1) and as detailed in Sections 5.4.1-5.4.4 (with exceptions noted). **Table 5.8** lists the analyses that were performed during baseline events. **Table 5.8** also details the methods used for each analysis, the groundwater volume, and the preservation technique. Sampling was performed by Shaw personnel as summarized below and described in more detail in **Appendix B** (Quality Assurance Project Plan; QAPP). Analysis of chloride, bromide, nitrate, nitrite, and sulfate by EPA Method 300.0 and TOC by EPA Method 415.1 was performed by the Shaw's New Jersey Certified Analytical Laboratory in Lawrenceville, NJ. Analysis of dissolved manganese and iron by EPA Method 200.7 was performed by ChemTech Laboratories, Mountainside, NJ under subcontract to Shaw. Analysis of explosives by EPA Method 8330 including key explosive degradation intermediates was conducted by the Severn Trent Laboratory (STL) in Knoxville, TN.

5.5.2 Sample Processing

The methods and procedures to be used in processing all samples related to pre-demonstration and demonstration activities are summarized below. After the well is parameters are stabilized during low flow sampling to EPA method guidelines (http://www.epa.gov/region9/qa/ pdfs/finalsopls1217.pdf), bottles were filled for each analysis as follows:

(1) Two 1L glass sample bottles without any chemical preservatives with Teflon-lined caps were filled directly from the groundwater stream for analysis of explosives (EPA method 8330). The bottles were filled to the neck with a small headspace. The bottles were then capped and placed on adequate ice for shipment.

(2) One 100-ml sample jar (plastic, no chemical preservatives) was filled to the top with water. The jar was then capped and placed on ice for shipment. This sample was used for analysis of anions by EPA Method 300 (nitrate, nitrite, sulfate, chloride, bromide).

(3) One 40-mL glass VOA vial preserved with phosphoric acid was filled to the top with water, capped, and placed on ice for shipment. This sample was used for analysis of Total Organic Carbon (TOC) (EPA Method 415.1).

(4) At select sampling points, a second VOA preserved with hydrochloric acid was filled to the top with groundwater without any headspace for analysis of alkane gases via EPA method 3810.

(5) At select sampling points, a 500-ml amber glass jar preserved with nitric acid was filled for analysis of total iron and manganese (EPA method 200.7).

Analyses 4 and 5 were performed only during selected sampling events to evaluate mobilization of metals and presence of dissolved gases in groundwater, respectively. Sample bottles for explosives analysis were prepared by Severn Trent Laboratories. Sample bottles for anions and metals were prepared at the Shaw Environmental Laboratory in Lawrenceville, NJ.

5.5.3 Sample Containers

The type and size of the sample container(s) for each analyte are listed in **Table 5.8**. All glass bottles had Teflon® caps. Clean glass bottles (1 L) were used for explosives. Clean plastic bottles (100 ml) were used for anions (nitrate, bromide, sulfate, chloride). Clean 40 mL VOA vials were used for TOC and dissolved gases, and clean 500 mL glass bottles were used for metals (iron and manganese, respectively).

5.5.4 Sample Preservation

The preservation techniques and conditions are listed in **Table 5.8**. The samples were chilled in coolers immediately after collection. Coolers were kept out of direct sunlight as much as

possible. The samples were stored at less than 4°C in a cooler or refrigerator before shipment to the analytical laboratories.

5.5.5 Sample Packaging and Shipment

Samples for laboratory analysis were packed in cleaned coolers with several ice packs. Shock absorbent packing was added to the cooler to prevent breakage or damage of the sample containers. A chain-of-custody (COC) form, sealed in a plastic bag to protect it from water, was securely taped to the inside lid of the cooler. An example of a completed COC form is provided in **Figure 5.27**.

The Field Engineer doing the sampling filled out and signed the COC prior to closing each cooler. Samples were shipped on the day of collection when possible or stored on ice or in a refrigerator prior to shipping. The samplers relinquished custody of the coolers to an express carrier to have them delivered to the off-site laboratories overnight. Upon receipt of each sample shipment, the coolers were inspected and any problems were noted on the COC record and reported to the QA staff person.

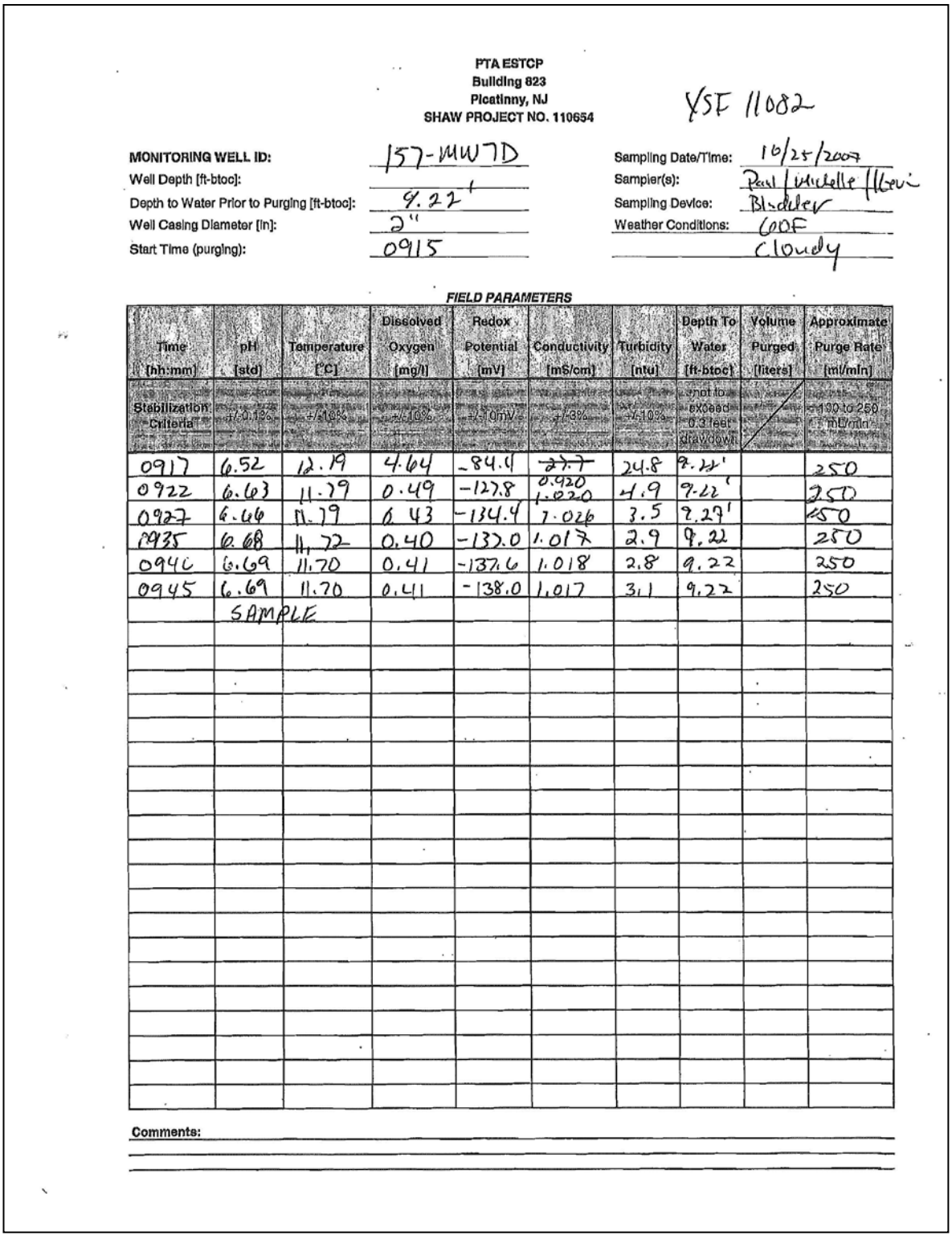
5.5.6 Quality Control

A Quality Assurance Project Plan (QAPP) prepared for project is provided as **Appendix B**. Additional details on project QA/QC are provided in the QAPP.

Table 5.8. Sampling Parameters, Preservatives, and Analytical Methods.

Parameter	Method/Procedure	**Preservative**	**Bottle Size**
Nitrate	EPA 300.0	4°C	100 mL[1]
Sulfate	EPA 300.0	4°C	100 mL[1]
Nitrite	EPA 300.0	4°C	100 mL[1]
Chloride	EPA 300.0	4°C	100 mL[1]
Bromide	EPA 300.0	4°C	100 mL[1]
Total Organic Carbon (TOC)	EPA 415.1	Phosphoric Acid	40 mL VOA
Total Manganese	EPA 200.7	Nitric Acid	500 mL[2,4]
Total Iron	EPA 200.7	Nitric Acid	500 mL[2,4]
Explosives (TNT, HMX, RDX) and degradation products (MNX, DNX, TNX, 2-ADNT, 4-ADNT, 2,4-DNT, 2,6-DNT, 2,4-DANT, 2,6-DANT)	EPA 8330	4°C	1000 mL[3]
Methane, ethane, ethene, propane	EPA 3810, RSK-175	Hydrochloric acid	40 mL VOA
Redox Potential	Field Meter	--	--
Dissolved Oxygen	Field Meter	--	--
pH	Field Meter	--	--
Conductivity	Field Meter	--	--

[1] The same sample bottle will be used for the analyses noted.
[2] The same sample bottle will be used for all analyses noted.
[3] The same sample bottle will be used for all analyses noted.
[4] Performed for only selected wells and sampling events.



PTA ESTCP
Building 823
Picatinny, NJ
SHAW PROJECT NO. 110654

YSF 11082

MONITORING WELL ID: 157-MW7D
Well Depth [ft-btoc]:
Depth to Water Prior to Purging [ft-btoc]: 9.22'
Well Casing Diameter [in]: 2"
Start Time (purging): 0915

Sampling Date/Time: 10/25/2007
Sampler(s): Paul / Michelle Hlavinka
Sampling Device: Bladder
Weather Conditions: 60F Cloudy

FIELD PARAMETERS

Time [hh:mm]	pH [std]	Temperature [°C]	Dissolved Oxygen [mg/l]	Redox Potential [mV]	Conductivity [mS/cm]	Turbidity [ntu]	Depth To Water [ft-btoc]	Volume Purged [liters]	Approximate Purge Rate [ml/min]
Stabilization Criteria	+/- 0.1%	+/-10%	+/- 10%	+/-10mV	+/-3%	+/-10%	not to exceed 0.3 feet drawdown		100 to 250 mL/min
0917	6.52	12.19	4.64	-84.1	~~27.7~~	24.8	9.22'		250
0922	6.63	11.79	0.49	-127.8	0.920 1.020	4.9	9.22'		250
0927	6.66	11.79	0.43	-134.4	1.026	3.5	9.27'		250
0935	6.68	11.72	0.40	-132.0	1.017	2.9	9.22		250
0940	6.69	11.70	0.41	-137.6	1.018	2.8	9.22		250
0945	6.69	11.70	0.41	-138.0	1.017	3.1	9.22		250
	SAMPLE								

Comments:

Figure 5.26. Example of field sheet used to document low-flow sampling and field parameters.

Shaw
17 Princess Rd
Lawrenceville, NJ 08648
609-895-5370/ 609-895-1858
Shaw Environmental and Infrastructure Inc.

7735 (Lab ID # (lab use))

CHAIN OF CUSTODY

Ref. Document # ____________ ____

Page 1 of 2

Project Contact: Paul Hatzinger (Name & phone #)

Send Report To: Michelle Lobsiger
Phone/Fax Number: (973) 770-5313
Address: 111 Howard Blvd, Suite 110
City/State: Mt. Arlington, NJ 07856

Sampler's Name(s): ____________

Project Number/Cost code: 110654 / 01080000
Project Name / Location: ESTCP / PTA
Purchase Order #: ____________
Shipment Date: 7/31/07
Waybill/Airbill Number: ____________
Lab Destination: Lawrenceville
Lab Contact Name / ph. #: Randi Rothmel

Lab No.	Sample ID Number	Sample Description	Collection Information: Date	Time	G/C	Matrix	# of containers	Container size	Preservative: HCL	NaOH	HNO_3	H_2SO_4	Ice	H_3PO_4	Analyses Requested: TOC	Mn, Fe	Anions	pH				Any Additional Information	Turn Around Time Requested
1	157MW-1	groundwater	7/31/07	1630	G	AQ	4	2 VOA, 1 50mL, 1 250mL			1		1	2	X	X	X	X					
2	157MW-1D	↓	↓	1735	↓	↓	↓	↓			↓		↓	↓	↓	↓	↓	↓					
3	157MW-2	↓	↓	1550	↓	↓	↓	↓			↓		↓	↓	↓	↓	↓	↓					
4	157MW-3	↓	↓	1455	↓	↓	↓	↓			↓		↓	↓	↓	↓	↓	↓					
5	157MW-4	↓	↓	1115	↓	↓	↓	↓			↓		↓	↓	↓	↓	↓	↓					
6	157MW-5	↓	↓	1000	↓	↓	↓	↓			↓		↓	↓	↓	↓	↓	↓					
7	157MW-6S	↓	↓	1440	↓	↓	↓	↓			↓		↓	↓	↓	↓	↓	↓					
8	157MW-6D	↓	↓	1350	↓	↓	↓	↓			↓		↓	↓	↓	↓	↓	↓					
9	157MW-7S	↓	↓	1145	↓	↓	↓	↓			↓		↓	↓	↓	↓	↓	↓					
10	157MW-7D	↓	↓	1025	↓	↓	↓	↓			↓		↓	↓	↓	↓	↓	↓					

Special Instructions:
please take pH of samples using anion bottle *

Known Waste Stream Circle:
RCRA PCB/dioxin PAH/oil RAD Corrosive Flammable Reactive

QC/Data Package Level Required:
I II III IV NJ EDD GIS EDD Preliminary data

G/C Codes
C = Composite G = Grab

QC Package Codes
Level I = data summary
Level II = data summary + basic QC
Level III = New Jersey QC reduced deliverable
Level IV = Full deliverable CLP package

Relinquished By:	Date / Time	Received By:	Date / Time
[signature]	Date: 7/31/07 Time: 1825	[signature]	Date: 8/1/07 Time: 1300
	Date: Time:		Date: Time:
	Date: Time:		Date: Time:

Cooler temperature upon arrival at Lab:

000006

Figure 5.27. Example of completed chain-of-custody form used to ship samples to analytical laboratories.

Table 5.9. Total Samples Collected During the Project.

Parameter	Baseline	Operational	Rebound	Total
EPA 300.0 Anions	80	89	36	205
Total Organic Carbon (TOC)	27	86	14	127
Total Iron and Manganese	12	28	28	68
Explosives	52	84	36	172
Methane, ethane, ethene	0	23	21	44
Field Parameters	78	84	36	198
Total	249	394	171	814

5.6 Sampling Results

The complete sampling results for the project are provided in this section. As shown in **Figure 5.28**, monitoring wells 157MW-4, 157MW-5, 157MW-6S, 157MW-6D, 157MW-7S, and 157MW-7D are treatment zone monitoring wells (TZMWs) because each was anticipated to be impacted by the recirculation system based on modeling results (Section 5.2.6), and to receive significant cheese whey during the period of system operation. The remaining 6 wells are upgradient (157 MW-1, 157MW-2 and 157-MW-3), below (bedrock well 157 MW-1D), or downgradient (157MW-8S and 157MW-8D) of the treatment area, presuming a slight southwesterly flow of groundwater as was indicated during various groundwater elevation mapping events. These wells serve as control wells to assess changes in contaminant concentrations outside of the treatment area. Based on model simulations, downgradient wells 157MW-8S and 157MW-8D may have been impacted by the treatment system after several months of "active-passive" operation. However, this assumed a 3 days on and 15 days off schedule, which was modified during the demonstration based upon the high overall TOC levels in the plot and observed rates of explosive degradation. Also, based on model results, upgradient well 157MW-3 should have been impacted by cheese whey after several months of operation, but due to the operational schedule, the well was not impacted and thus served as a third upgradient control well. As detailed previously in Section 5.4.3, the system was operated far less frequently than originally modeled, thus reducing costs and system O&M. However, because of this operational mode, the zone of impact of the system did not reach 157-MW8S, 157MW-8D, or 157MW-3 during the demonstration period.

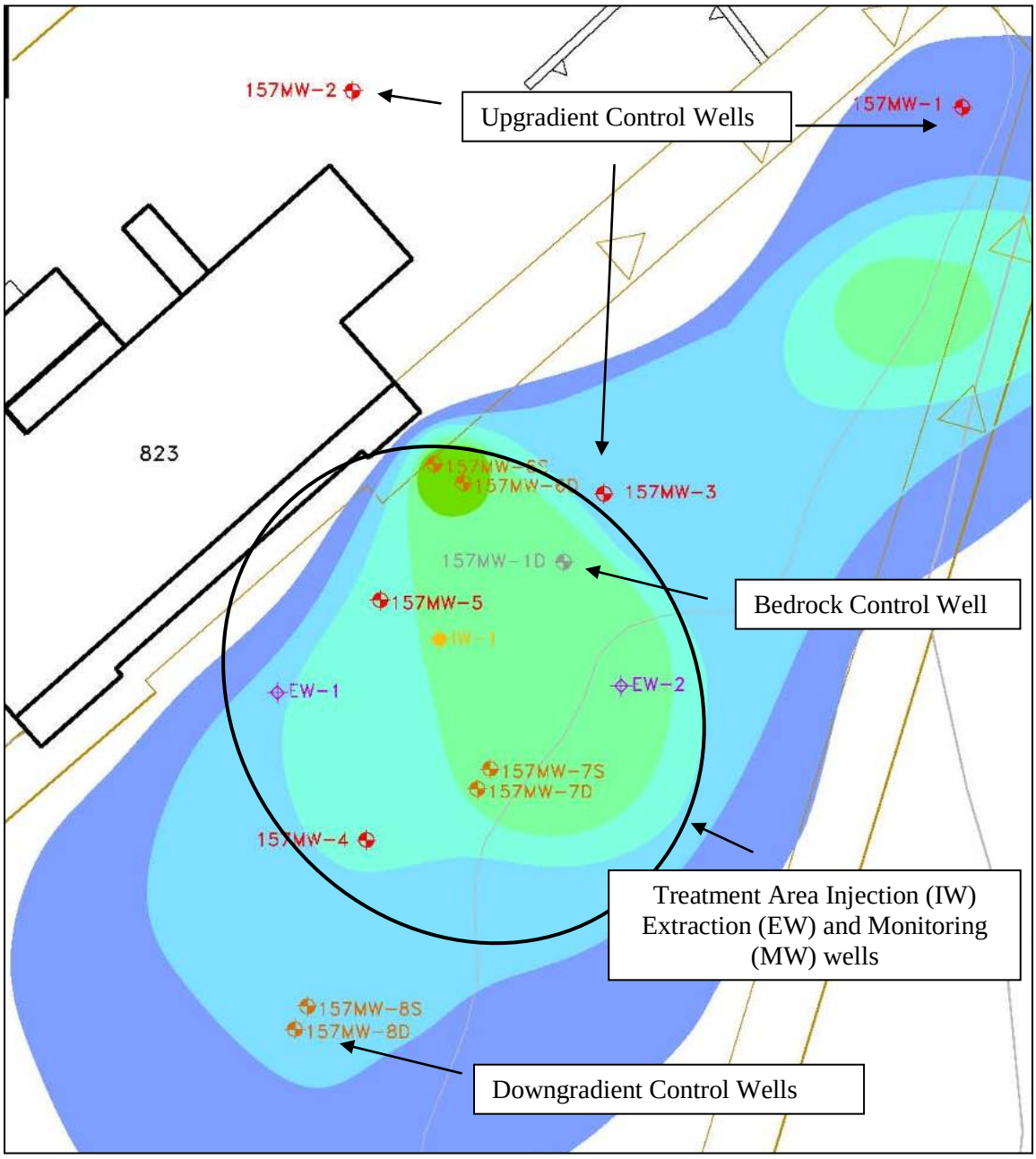


Figure 5.28. Layout of test plot wells with treatment wells. Shaded areas represent estimated RDX concentrations at the beginning of the demonstration.

5.6.1 Total Organic Carbon (TOC)

TOC analysis was utilized as a measure of cheese whey distribution in the aquifer. Based on laboratory measurements, the dissolved TOC resulting from cheese whey was ~ 1/3 of the mass of whey added to solution (i.e., if powdered cheese whey was added at 50 g/L, the resulting TOC was 16.5 g/L) (**Figure 5.29**). A significant increase in TOC concentration within the treatment zone was observed following the initial system operation and injection of cheese whey (corresponding to Day 0) (**Figure 5.30 and Table 5.10**). TOC in all wells in the treatment zone quickly reached concentrations exceeding 90 mg/L after the initial injection, with some wells exceeding 200 mg/L. TOC in monitoring wells outside of the treatment zone did not increase above the background concentration of ~ 2 mg/L (**Table 5.10**). The initial rate of TOC decline after the first injection varied from ~ 2.2 to 4.5 mg /day (Day 15-Day 33). Significant increases in TOC were again observed after the third and fourth injection events in all wells except 157-MW6S and 157MW-6D. These wells were upgradient of the injection well, and it is presumed that they were not impacted by the later whey additions due to an increased rate of groundwater flow in the area. The gradient in the treatment area was relatively flat and prone to slight alterations with the water table as previously discussed in Section 5.2.2.2. The depth to water in the treatment plot declined by ~ 2 ft between Day 100 and Day 222, consistent with high rainfall in the region during this period. This change is likely to have impacted upgradient distribution of injected cheese whey during the final two events.

5.6.2 Explosives and Degradation Products

5.6.2.1 TNT and Intermediates

TNT concentrations in the treatment zone monitoring wells declined rapidly after the initial cheese whey addition (**Figure 5.31 and Table 5.11**). TNT concentrations were below analytical detection limits (PQL = 0.25 μg/L) in all of the treatment zone monitoring wells (TMZWs) by Day 62 of the study, and remained at or below this concentration in all TZMWs except 157MW-6S throughout the remainder of the demonstration. In Well 157MW-6S, which was not impacted significantly by cheese whey additions after the first event and second events, and reached background TOC levels by Day 222 (see TOC values in Table 5.8), TNT was detected at 6.3 μg/L on Day 222, from a starting concentration of 310 μg/L. The TNT in this well had declined back to 0.39 μg/L by the end of rebound sampling on Day 420. TNT concentrations in upgradient and downgradient monitoring wells, as well as the deep bedrock well 157MW-1D, were largely unaffected by system operation. An increase in the concentration of TNT from 16 to 130 μg/L was observed in control Well 157MW-3, which is just upgradient of the treatment zone. This increase probably reflects mobilization of TNT from soils in the region during rainfall events. Overall, the data reveal that the treatment system was highly effective at reducing TNT concentrations in the treatment zone.

Two common TNT daughter products, 4-amino-4,6-dinitrotoluene (4-ADNT) **(Table 5.12 and Figure 5.32)** and 2-amino-2,6-dinitrotoluene (4-ADNT) **(Table 5.13 and Figure 5.33)** were present from ~ 1 to 120 μg/L in groundwater monitoring wells at the demonstration site. These

products are formed from an initial reduction of one nitro-group on TNT to an amino group, and may either have been present in the water released from the facility during processing, or have formed after disposal to land surface via biological reactions (Walker and Kaplan, 1992). A rapid reduction in the concentrations of both of these compounds in groundwater was observed following injection of cheese whey. In fact, neither TNT daughter product was present above the analytical PQL of 0.25 μg/L in the TZMWs by Day 148. There was a slight rebound of these compounds in upgradient wells 157MW-6S and 157MW-6D after this time, but each of these wells was not impacted by cheese whey after the initial two injections in Day 0 and Day 41, as evidenced by the low TOC in each by Day 222 **(Table 5.10)**. For each of the other TZMWs, levels of these compounds remained below detection (< 0.25 μg/L) from Day 148 to Day 420. There was no appreciable increase or decrease in the concentration of these compounds in the wells outside of the treatment zone.

With the exception of one detection in well 157MW-5, 2,4-diamino-6-nitrotoluene (2,4-DANT) **(Table 5.14 and Figure 5.34)** and 2,6-diamino-4-nitrotoluene (2,4-DANT) **(Table 5.15** and **Figure 5.35)** were not present in Picatinny groundwater prior to whey injection. These compounds, each of which is an expected degradation intermediate of TNT, increased in the TZMWs as TNT biodegraded and then declined in concentration to below their respective PQL values by Day 98 and for the duration of the demonstration in TZMWs 157MW-4, 157MW-5 157MW-7S and 157MW-7D**.** The compounds declined and then rebounded in Well 167MW-6S once all the TOC from cheese whey was depleted. These partially reduced derivatives of TNT can polymerize with each other and with other organic compounds, producing polymers with low solubility and toxicity (Pennington et al., 1997). In addition, TNT can ultimately be reduced to 2,4,6-triaminotoluene (2,4,6-TAT). This compound binds strongly and irreversibly to humics and other natural organics in aquifers, thus completely detoxifying TNT. Thus, through biological reduction, TNT is not mineralized but rather reduced to derivatives that irreversibly polymerize and/or bind to natural organics, thus rendering them permanently sequestered (Pennington, 1995, 1997; Hawari et al., 2000a).

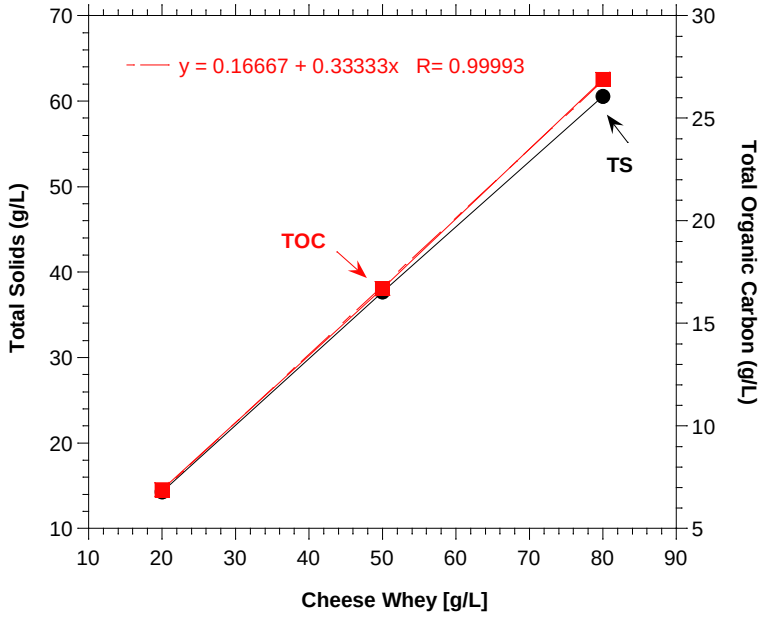


Figure 5.29. Comparison of total cheese whey added to solution with total organic carbon (TOC) and total solids (TS).

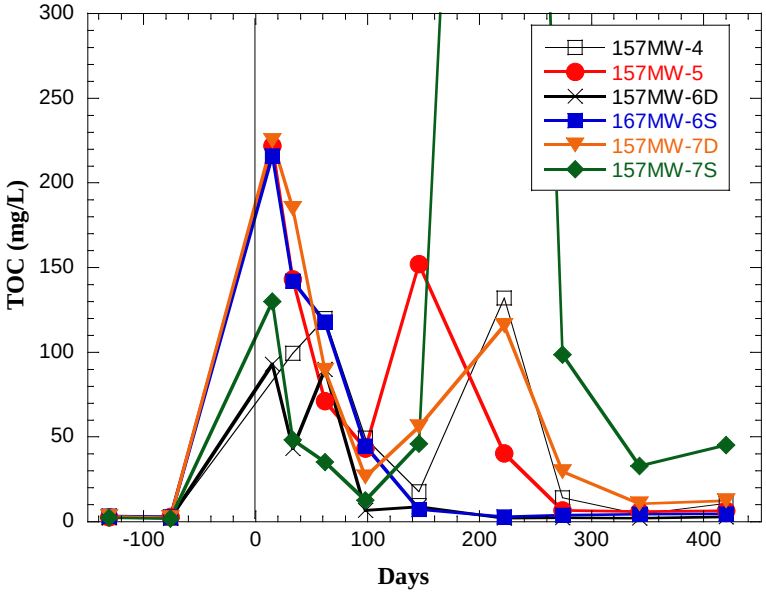


Figure 5.30. TOC concentrations in treatment plot monitoring wells during the demonstration. Whey was injected as indicated by the arrows. Values for control wells are not provided.

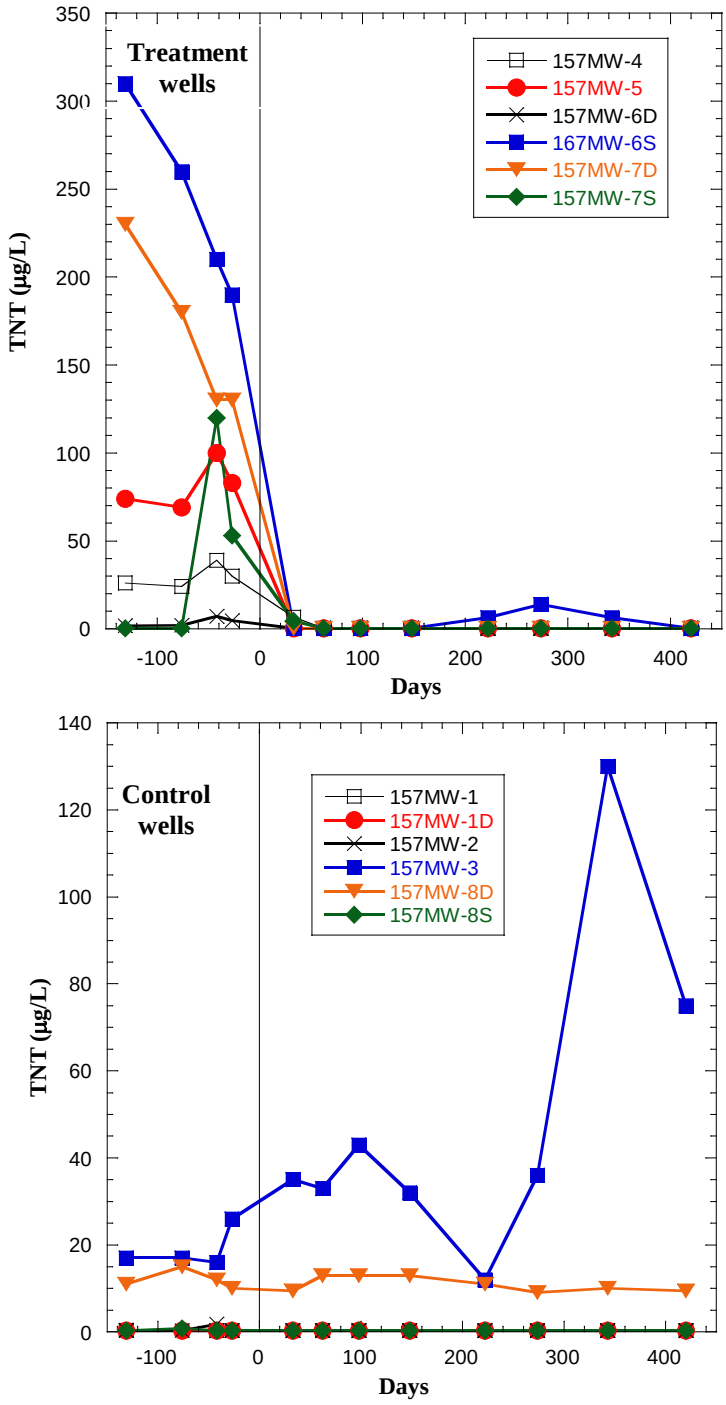


Figure 5.31. TNT concentrations in treatment zone monitoring wells (top panel) and the control wells (bottom panel) during the demonstration. The initial cheese whey injection occurred at Day 0.

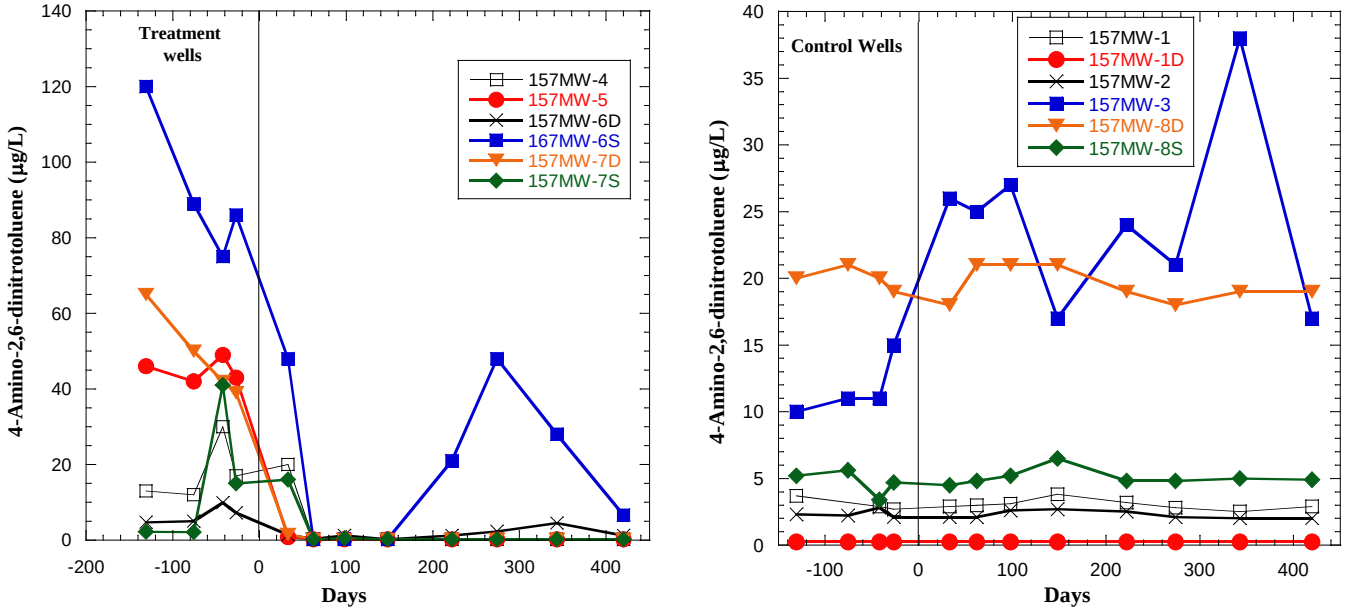


Figure 5.32. Concentrations of 4-amino-2,6-dinotrotoluene in treatment zone monitoring wells (left panel) and control wells (bottom panel) during the demonstration. The initial cheese whey injection occurred at Day 0.

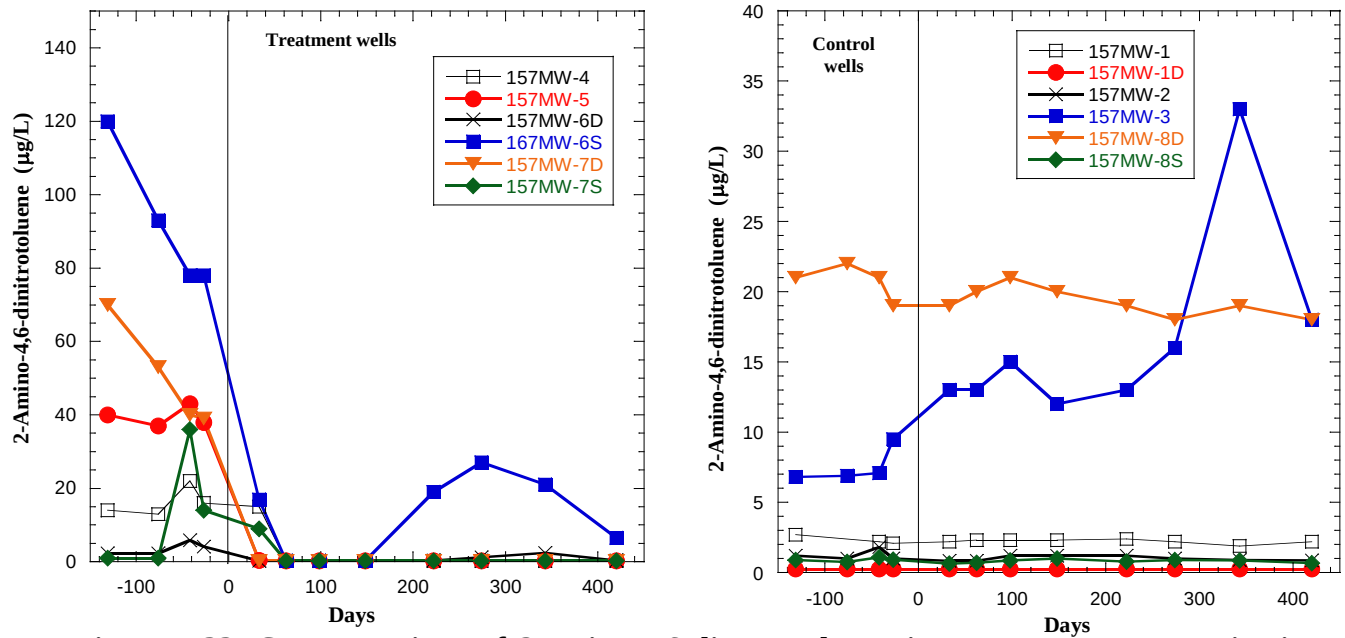


Figure 5.33. Concentrations of 2-amino-4,6-dinotrotoluene in treatment zone monitoring wells (left panel) and control wells (bottom panel) during the demonstration. The initial cheese whey injection occurred at Day 0.

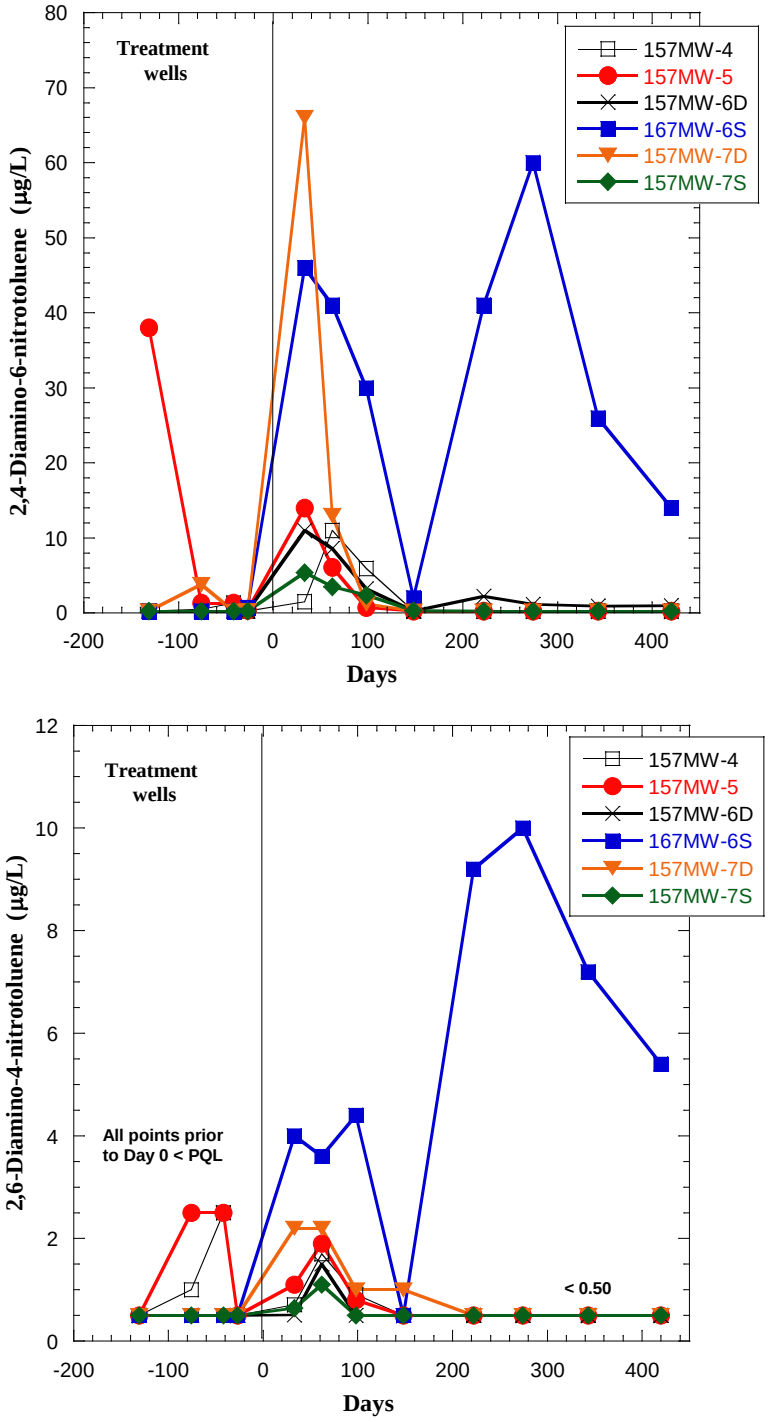


Figure 5.34. Concentrations of 2,4-diamino-6,nitrotoluene (top panel) and 2,6-diamino-4-nitrotoluene (bottom panel) in treatment zone monitoring wells. These compounds were < PQL (generally 0.25 ug/L) in control wells during the demonstration.

Table 5.10. TOC Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue are data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	2.98	2.97	2.14	2.83	2.34	2.66	2.59	3.40	2.99	2.47	2.08	1.97
03/15/07	-76	3.90	6.59	ND[1]	2.77	2.17	3.06	2.17	2.76	2.07	2.79	2.38	1.81	2.05	1.77
6/6/2007	7	61.8	6.12	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]
6/14/2007	15	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	222	93.0	216	225	130	ND[1]	ND[1]
7/2/2007	33	65.0	29.7	3.71	2.11	2.00	2.10	99.5	143	43.3	142	185	48.2	2.49	3.87
7/31/2007	62	33.2	23.2	5.31	2.51	1.97	1.31	120	71.1	89.9	118	89.3	35.2	2.95	4.27
9/5/2007	98	16.9	12.0	3.40	3.43	3.12	3.68	49.4	43.1	6.66	44.7	26.4	12.7	2.63	2.58
10/25/2007	148	53.1	24.6	2.59	2.48	2.27	2.76	17.8	152	8.85	7.21	56.1	46.1	2.60	2.14
1/7/2008	222	13.3	69.5	2.87	1.28	0.99	1.42	132	40.5	2.20	2.87	116	1060	1.30	1.86
2/28/2008	274	3.06	18.1	2.61	2.88	2.70	2.71	14.2	6.69	2.45	3.81	29.7	98.6	2.43	2.42
5/7/2008	343	10.9	11.4	1.71	1.47	1.99	1.70	4.45	5.95	2.23	4.39	10.7	32.8	1.45	1.21
7/23/2008	420	ND[1]	ND[1]	4.90	3.07	3.43	2.53	10.9	6.41	2.81	4.69	12.3	45.3	1.99	2.21
12/15/2008	565	ND[1]	ND[1]	3.53	ND[1]	3.84	ND[1]	5.86	4.17	<1	ND[1]	14.9	29.7	2.59	ND[1]

[1]ND, Not Determined

Table 5.11. TNT Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	0.42	<0.25	<0.25	17	26	74	1.6	310	230	<0.25	11	<0.25
03/15/07	-76	3.5	170	ND[1]	<0.25	<0.25	17	24	69	1.9	260	180	<0.25	15	<0.75
04/18/07	-42	ND[1]	ND[1]	0.33	<0.25	<1.8	16	39	100	7.0	210	130	120	12	<0.25
5/3/2007	-27	1.1	91	0.30	<0.25	<0.25	26	30	83	4.6	190	130	53	10	<0.25
7/2/2007	33	<0.25	39	0.26	<0.25	<0.25	35	6.5	<0.25	<0.25	<0.25	<0.25	4.4	9.5	<0.25
7/31/2007	62	<0.25	15	<0.25	<0.25	<0.25	33	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	13	<0.25
9/5/2007	98	<0.25	0.41	0.27	<0.25	<0.25	43	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	13	<0.25
10/25/2007	148	<0.25	<0.25	<0.25	<0.25	<0.25	32	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	13	<0.25
1/7/2008	222	<0.25	<0.25	<0.25	<0.25	<0.25	12	<0.25	<0.25	<0.25	6.3	<0.25	<0.25	11	<0.25
2/28/2008	274	<0.25	<0.25	<0.25	<0.25	<0.25	36	<0.25	<0.25	<0.25	14	<0.25	<0.25	9.1	<0.25
5/7/2008	343	<0.25	<0.25	<0.25	<0.25	<0.25	130	<0.25	<0.25	0.29	6.3	<0.25	<0.25	10	<0.25
7/23/2008	420	<0.25	<0.25	<0.25	<0.25	<0.25	75	<0.25	<0.25	<0.25	0.39	<0.25	<0.25	9.5	<0.25

[1]ND, Not Determined

Table 5.12. 2-Amino-4,6-dinotrotoluene Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	2.7	<0.25	1.2	6.8	14	40	2.3	120	70	1.0	21	0.84
03/15/07	-76	6.7	49	ND[1]	<0.25	1.0	6.9	13	37	2.3	93	53	1.0	22	<0.75
04/18/07	-42	ND[1]	ND[1]	2.2	<0.25	<1.8	7.1	22	43	5.8	78	40	36	21	1.1
5/3/2007	-27	6.0	33	2.1	<0.25	1.0	9.5	16	38	4.1	78	39	14	19	0.93
7/2/2007	33	1.2	35	2.2	<0.25	0.84	13	15	0.37	<0.25	17	0.25	9.0	19	0.65
7/31/2007	62	<0.25	12	2.3	<0.25	0.84	13	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	20	0.69
9/5/2007	98	0.94	1.4	2.3	<0.25	1.2	15	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	21	0.86
10/25/2007	148	<0.25	<0.25	2.3	<0.25	1.2	12	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	20	1.0
1/7/2008	222	<0.25	<0.25	2.4	<0.25	1.2	13	<0.25	<0.25	0.39	19	<0.25	<0.25	19	0.78
2/28/2008	274	1.5	<0.25	2.2	<0.25	1.0	16	<0.25	<0.25	1.2	27	<0.25	<0.25	18	0.90
5/7/2008	343	1.3	1.4	1.9	<0.25	0.89	33	<0.25	<0.25	2.4	21	<0.25	<0.25	19	0.85
7/23/2008	420	ND[1]	ND[1]	2.2	<0.25	0.87	18	<0.25	<0.25	0.39	6.5	<0.25	<0.25	18	0.66

[1]ND, Not Determined

Table 5.13. 4-Amino-2,6-dinotrotoluene Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	3.7	<0.25	2.3	10	13	46	4.7	120	65	2.2	20	5.2
03/15/07	-76	7.7	49	ND[1]	<0.25	2.2	11	12	42	5.0	89	50	2.1	21	5.6
04/18/07	-42	ND[1]	ND[1]	2.9	<0.25	2.8	11	30	49	9.9	75	42	41	20	3.4
5/3/2007	-27	8.6	37	2.7	<0.25	2.1	15	17	43	7.2	86	39	15	19	4.7
7/2/2007	33	3.9	56	2.9	<0.25	2.1	26	20	0.87	1.4	48	1.5	16	18	4.5
7/31/2007	62	0.47	22	3.0	<0.25	2.1	25	<0.25	<0.25	0.30	<0.25	<0.25	<0.25	21	4.8
9/5/2007	98	2.0	3.9	3.1	<0.25	2.6	27	<0.25	<0.25	1.2	0.35	<0.25	0.52	21	5.2
10/25/2007	148	<0.25	<0.25	3.8	<0.25	2.7	17	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	21	6.5
1/7/2008	222	0.82	<0.25	3.2	<0.25	2.5	24	<0.25	<0.25	1.2	21	<0.25	<0.25	19	4.8
2/28/2008	274	2.2	<0.25	2.8	<0.25	2.1	21	<0.25	<0.25	2.3	48	<0.25	<0.25	18	4.8
5/7/2008	343	1.6	<0.25	2.5	<0.25	2.0	38	<0.25	<0.25	4.5	28	<0.25	<0.25	19	5.0
7/23/2008	420	ND[1]	<0.25	2.9	<0.25	2.0	17	<0.25	<0.25	1.2	6.6	<0.25	<0.25	19	4.9

[1]ND, Not Determined

Table 5.14. 2,4-Diamino-6-nitrotoluene Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.25	<0.25	<0.25	<0.25	<0.25	**38**	<0.25	<100	<0.25	<0.25	<0.25	<0.25
03/15/07	-76	<0.25	<3.8		<0.25	<0.25	<0.25	<0.5	<1.3	<0.25	<5	<3.8	<0.25	<1.3	<0.75
04/18/07	-42	ND[1]	ND[1]	<0.25	<0.25	<1.8	<0.25	<1.3	<1.3	<0.25	<0.25	<0.25	<0.25	<1.3	<0.25
5/3/2007	-27	<0.25	**1.1***	<0.25	<0.25	<0.25	<0.25	<0.25	**0.37***	<0.25	**0.71***	**0.34***	<0.25	0.36	<0.25
7/2/2007	33	**10**	**4.5**	<0.25	<0.25	<0.25	<0.25	**1.5**	**14**	**11**	**46**	**66**	**5.4**	<0.25	<0.25
7/31/2007	62	**4.2**	**14**	<0.25	<0.25	<0.25	<0.25	**11**	**6.1**	**8.6**	**41**	**13**	**3.5**	<0.25	<0.25
9/5/2007	98	**0.86**	**9.7**	<0.25	<0.25	<0.25	<0.25	**5.9**	**0.74**	**3.2**	**30**	**1.2**	**2.4**	<0.25	<0.25
10/25/2007	148	**0.69**	**8.5**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**2.0**	<0.25	**0.34**	<0.25	<0.25
1/7/2008	222	**2.0**	**0.66**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**2.2**	**41**	<0.25	<0.25	<0.25	<0.25
2/28/2008	274	**1.7**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**1.1**	**60**	<0.25	<0.25	<0.25	<0.25
5/7/2008	343	**0.78**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.86**	**26**	<0.25	<0.25	**17**	<0.25
7/23/2008	420	ND[1]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.94**	**14**	<0.25	<0.25	<0.25	<0.25

[1]ND, Not Determined

*Value exceeds highest calibration standard by >15%

Table 5.15. 2,6-Diamino-4-nitrotoluene Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
03/15/07	-76	<0.5	<7.5	ND[1]	<0.5	<0.5	<0.5	<1	<2.5	<0.5	<10	<7.5	<0.5	<2.5	<1.5
04/18/07	-42	ND[1]	ND[1]	<0.5	<0.5	<3.5	<0.5	<2.5	<2.5	<0.5	<0.5	<0.5	<0.5	<2.5	<0.5
5/3/2007	-27	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
7/2/2007	33	**1.0**	<0.5	<0.5	<0.5	<0.5	<0.5	**0.71**	**1.1**	**0.51**	**4.0**	**2.2**	**0.64**	<0.5	<0.5
7/31/2007	62	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	**1.7**	**1.9**	**1.5**	**3.6**	**2.2**	**1.1**	<0.5	<0.5
9/5/2007	98	<0.5	**0.93**	<0.5	<0.5	<0.5	<0.5	**0.91**	**0.80**	**0.50**	**4.4**	**1.0**	<0.5	<0.5	<0.5
10/25/2007	148	<0.5	**0.73**	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	**1.0**	<0.5	<0.5	<0.5
1/7/2008	222	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	**9.2**	<0.5	<0.5	<0.5	<0.5
2/28/2008	274	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	**10**	<0.5	<0.5	<0.5	<0.5
5/7/2008	343	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	**7.2**	<0.5	<0.5	<0.5	<0.5
7/23/2008	420	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	**5.4**	<0.5	<0.5	<0.5	<0.5

[1]ND, Not Determined

[#]Results reported are from the phenyl hexyl confirmation column for Method 8330 because TNX and 2,6-Diamino-4-nitrotoluene were reported to co-elute on the LC-18 (i.e., reporting) column.

5.6.2.2 RDX and Degradation Intermediates

RDX biodegradation occurred somewhat more slowly than for TNT as expected based on previous laboratory microcosm and column studies. However, 148 days after the initial injection of cheese whey, RDX concentrations were ≤ 5 μg/L in all 6 of the TZMWs, and concentrations in 5 of these wells were < 1.5 μg/L **(Figure 5.35 and Table 5.16).** The TZMWs had RDX concentrations ranging from 5 μg/L to 170 μg/L during the final baseline sampling event (Day -27), with a median value of 66 μg/L. From Day 222 to Day 565, the concentration of RDX in all of the downgradient TZMWs (157MW-4, 157MW-5, 157MW-7S, 157MW-7D) remained < 1 μg/L. Thus, more than one year after the final injection of cheese whey (Day 181), RDX was < 1 μg/L throughout the downgradient region of the treatment plot. Upgradient TZMWs 157MW-6S and 157MW-6D also reached < 1 μg/L on Day 148. However, as previously noted, this well pair was not impacted by cheese whey after the initial two injections on Days 0 and Day 41, presumably due to an increased rate of groundwater flow in the plot area. As the TOC from cheese whey declined during the course of the study, the RDX rebounded somewhat in both wells. In those wells where TOC from cheese whey remained above ~ 5 mg/L, rebound was not observed. A comparison of TOC vs. RDX for Well 157MW-6S (which showed rebound) and 157MW-7D (no rebound) is provided in **Figure 5.36.** The data clearly show that cheese whey effectively promoted RDX biodegradation throughout the treatment zone, and that as long as a minimal concentration of TOC was maintained, rebound did not occur.

During the sampling event at 148 days, the contract analytical laboratory performing 8330 analysis for explosives (*Severn Trent Laboratories* which later changes their name to *Test America*) reported analytical interference with RDX in the treatment wells with the highest TOC concentrations. It appears that one or more degradation products from the cheese whey elute near the region of RDX in the 8330 analysis and were falsely identified as RDX (i.e., false positive). The results of a photodiode array (PDA) scan on these samples further confirmed that the peak present via 8330 was not RDX as the shape of the peak in the sample and that of the RDX standard were different. Values from a confirmation column with a different packing material (phenyl hexyl column) were also appreciably higher than expected for treatment wells 157MW-4, 157MW-5, 157MW-7D based on initial concentrations in the aquifer and degradation trends to that point. In some instances, mg/L concentrations of RDX were reported due to the interfering compounds. No interference was reported for any of the wells outside of the treatment area.

Because of the analytical issues observed with samples from several of the TZMWs on Day 148 and for several events thereafter using EPA 8330 analysis, all extracts (after solid phase extraction) from samples exhibiting interference were reanalyzed with a second method utilizing liquid-chromatography/mass-spectrometry (LC/MS) in the laboratory of Dr. Jalal Hawari at the NRC Biotechnology Research Institute in Montreal, Canada. Dr. Hawari is one of the leading experts on the analysis of explosive compounds and intermediates. The sample extracts (obtained from the Test America laboratory after SPE and 8330 analysis) were re-analyzed by LC/MS using a Bruker bench-top microTOFQ mass detector attached to a Hewlett Packard 1200 Series HPLC system equipped with a DAD detector. The samples were injected into a 3.5 μm-pore size

Zorbax SB-C18 column (2.1 mm ID by 150 mm; Agilent, CA) at 25°C. The solvent system was composed of a CH_3CN/1 μM of TFA in water at a flow rate of 200 μL min^{-1}. A first gradient was run from 20 % to 40 % CH_3CN over 12 min and a second from 40 % to 80 % for 8 min. For mass analysis, negative electrospray ionization mode was used to produce a characteristic TFA fragment at m/z 113 from the adduct ions $[M+TFA]^-$. The mass range was scanned from 50 to 550 Da. Because of the MS analysis, RDX could be positively identified and quantified in the presence of other products from the cheese whey fermentation. The MDL values for RDX and HMX using this method were 0.01 mg/L and 0.02 mg/L, respectively, in the sample extracts. However, because the explosives were concentrated 50x via SPE prior to analysis, the MDL values were reduced accordingly to ~ 0.2 μg/L and 0.4 μg/L, respectively. Chromatographs of RDX and HMX in standards and samples using this approach are provided in **Figure 5.37**. The data obtained from the LC/MS method are denoted in **Table 5.16** with an "^" symbol. In the absence of LC/MS analysis, it would not have been possible to accurately determine the concentration of RDX or HMX in some of the TZMWs.

The RDX concentrations in the upgradient and downgradient CZMWs remained reasonably constant throughout the demonstration period, with the exception of a temporary increase in RDX at 157MW-3 (**Figure 5.35 and Table 5.16**). It is likely that this increase resulted from the flushing or RDX from soils or the vadose zone to the aquifer, since the nitramine was detected in both matrices during previous site assessment work (Gerdes et al., 2004). Moreover, the depth to water at the demonstration site declined by ~ 2 ft just prior to the observed increase in 157MW-3 (from Day 148 to Day 222) as a result of high rainfall in the area.

The concentrations of the RDX daughter products MNX, DNX, and TNX are provided in **Figure 5.36** and **Tables 5.17** to **5.19**. Each of these products increased in one or more of the TZMWs, but not in the CZMWs. However, the total concentrations were < 20 μg/L in all cases, and generally much lower, and all three nitroso-derivatives were transient. The production of these intermediates is expected during reductive biodegradation of the nitramine, and clearly indicates that the explosive is being biologically reduced in the treatment area wells. A significant decrease in the concentrations of each of these daughter products was observed during the demonstration, and all were near or below detection by Day 420 of groundwater monitoring. All three products remained below detection in wells sampled on Day 565. These data suggest that each of the RDX nitroso-derivatives were further biodegraded in the aquifer. Using the primary L18 column, TNX could not be easily separated from 2,6-diamino-4-nitrotoluene, a daughter product of TNT biodegradation. However, separation was better on the phenyl-hexyl confirmation column. As a result, the concentrations reported in **Figure 5.36** and **Table 5.19** for TNX are from the secondary column.

In addition to MNX, DNX and TNX, groundwater samples from eight of the Picatinny Wells (Wells 157MW-1D, 157MW-6S, and 157MW-8S were not sampled) were analyzed for products produced by bacteria after ring cleavage of RDX including methylene dinitramine (MEDINA), 4-nitro-2,4-diazabutanal (NDAB), nitrous oxide, and formaldehyde during sampling for SERDP Project ER-1607, in which preservation methods for these compounds were developed, and

testing was performed at several DoD installations with RDX in groundwater in order to assess the occurrence of RDX biodegradation under differing geochemical conditions (Paquet et al., 2011; Fuller and Hatzinger, *unpublished data*). The samples were collected on Day 199 of system operation (12/15/08). Neither MEDINA nor NDAB were detected in any of the system wells at this time even though significant RDX biodegradation was indicated in all of the TZMWs. Nitrous oxide was lower in the TZMWs and in Well 157MW-8D (< 2 to 6 μg/L), than in two of the two upgradient CZMWs (28 and 27 μg/L, in 157MW-1 and 157MW-2, respectively), suggesting that this gas did not accumulated during explosives degradation via cheese whey addition. Finally, concentrations of formaldehyde ranged from ~ 800 μg/L to > 4,000 μg/L in the TZMWs, compared to < 20 μg/L in the CZMWs. It is possible that a portion of the formaldehyde was derived from the degradation of RDX and HMX (as indicated in treatability studies). However, the high concentrations detected in some of the wells indicate that fermentation of cheese may have contributed much of the formaldehyde to groundwater, as unlike NDAB and MEDINA, formaldehyde has multiple sources in the environment. Moreover, in treatability studies, biodegradation of 2 μmol/L of RDX (~ 450 μg/L) produced only 2 μmol/L (~ 75 μg/L) of formaldehyde, which was transient. Thus, the data suggest that significant accumulation of ring cleavage products from RDX, including NDAB and MEDINA, during *in situ* RDX biodegradation via cheese whey addition is unlikely.

5.6.2.3 HMX

The LC/MS method used to analyze RDX in the presence of high TOC concentrations in the TZMWs, also was used for HMX in some samples due to analytical interference (see previous section). Degradation of HMX was not observed in any of the treatment wells during the initial two months of operation **(Figure 5.37** and **Table 5.20)**. During the laboratory microcosm studies conducted for the project, the lag period before HMX degradation occurred was longer than for either RDX or TNT, so the field data are consistent with the laboratory studies. However, an initial decline in this nitramine was noted in all of the TMZWs between Day 62 and Day 148. HMX concentrations continued to decline thereafter in all of the downgradient TZMWs (157MW-4, 157MW-5, 157MW-7S, 157MW-7D), and by Day 274, the HMX concentration in each of these wells was < 0.4 μg/L. A slight rebound was observed in Well 157MW-5 at Day 565 (384 days after the last injection) to 6.2 μg/L, but HMX was < 1 μg/L each of the other wells throughout the remainder of the study. HMX also declined initially in upgradient TZMW 157MW-6S, but rebounded quickly as the TOC concentration in this well declined to < 5 mg/L on Day 222. The HMX concentration in upgradient TZMW 157MW-6D reached 0.52 μg/L on Day 148, and then increased somewhat. However, HMX was < 3 μg/L from Day 222 to Day 343, and < 2 μg/L during the final sampling events at Day 420 and Day 565. Thus, as with RDX, the data from the downgradient TZMWs suggest that the addition of cheese whey to the Picatinny aquifer effectively promoted HMX biodegradation to sub μg/L concentrations. When TOC concentrations were maintained > 5 mg/L, rebound of HMX was not observed.

5.6.2.4 Other 8330 Nitroaromatics

A number of other nitroaromatic compounds were quantified via EPA 8330 analysis throughout the demonstration, including several nitrobenzenes and nitrotoluenes, 2,4,6-trinitrophenol (picric acid), 2,4,6-trinitrophenylmethylnitramine (Tetryl), and pentaerythritol tetranitrate (PETN). Among these compounds, 1,3,5-trinitrobenzene (1,3,5-TNB) was present throughout the demonstration plot at ~ 10 to 70 μg/L prior to cheese whey injection. A rapid decline in the concentrations of this compound was observed in all TZMWs. In fact, 1,3,5-TNB in all of the TZMWs was < 0.25 μg/L by Day 62, while the upgradient and downgradient CZMWs remained near baseline levels (**Figures 5.38 and Table 5.21**, respectively). The concentration of 1,3,5-trinitrobenzene was < 0.6 μg/L in all TZMWs from Day 62 until the final samples for this compound were collected on Day 420.

Among the other compounds detected in the treatment plot, 2,4-dinotrotoluene (2,4-DNT) and 2,6-dinotrotoluene (2,6-DNT) also appeared to be biologically degraded in the treatment zone wells. 2,4-DNT was detected consistently in wells 157MW-3, 157MW-5, 157MW-6D, 157MW-6S, 157MW-7D, and 157MW-8D during baseline sampling at concentrations ranging from ~ 0.5 to 1.7 μg/ L (0.25 μg/L PQL). The compound was not detected in any of the other wells, except the extraction wells during system operation. After cheese whey addition, 2,4-DNT declined to <0.25 μg/L in the TZMWs by Day 33, and with a few exceptions, remained below this concentration throughout the demonstration **(Figure 5.39 and Table 5.22)**. There was no apparent decline in 2,4-DNT in CZMWs 157MW-3 or 157MW-8D during the study. Similar results were observed for 2,6-DNT in the same wells **(Table 5.23)**. The compound, however, was not detected as consistently in the wells prior to system start-up, although each of the wells with 2,4-DNT had at least one detection during background sampling, and each of those that received cheese whey were below detection thereafter (< 0.25 μg/L) with the exception of one transient value of 1.0 μg/L in 157MW-6S on Day 343. By comparison, 2,6-DNT was detected in CZMWs 157MW-3 and 157MW-8D on several occasions during the course of the study.

The other compounds that were measured during each sampling event by EPA 8330 included 1,2-dinitrobenzene **(Table 5.24)**, 2-nitrotoluene **(Table 5.25)**, 3-nitrotoluene **(Table 5.26)**, 4-nitrotoluene **(Table 5.27)**, PETN **(Table 5.28)**, picric acid **(Table 5.29)**, and Tetryl **(Table 5.30)**. Overall, the occurrence of these compounds during baseline sampling and throughout the demonstration was too sporadic to determine the effectiveness of the cheese whey injection for treatment of each. The data are provided herein to document that each of these compounds was measured during the study.

5.6.2.5 Summary of Explosives Results

The key findings of this ESTCP demonstration with respect to explosives biodegradation are as follows: (1) anaerobic biodegradation of the key explosives impacting the Area 157 was stimulated by the injection and distribution of cheese whey in groundwater; (2) biodegradation of key explosives and intermediates including TNT, RDX, HMX, 2-DNT, 2,6-DNT, and 1,3,5-TNB to sub μg/L concentrations occurred; (3) degradation intermediates of TNT and RDX were detected, but these compounds were transient in cheese whey impacted wells; (4) rebound of

explosives occurred in wells once TOC from cheese whey reached low concentrations (i.e., < 5 mg/L), but not in wells in which cheese whey TOC remained elevated, and (5) TOC from cheese whey persisted for more than a year at concentrations sufficient to prevent rebound of explosives in the downgradient region of the demonstration plot. All critical performance objectives of this demonstration were met.

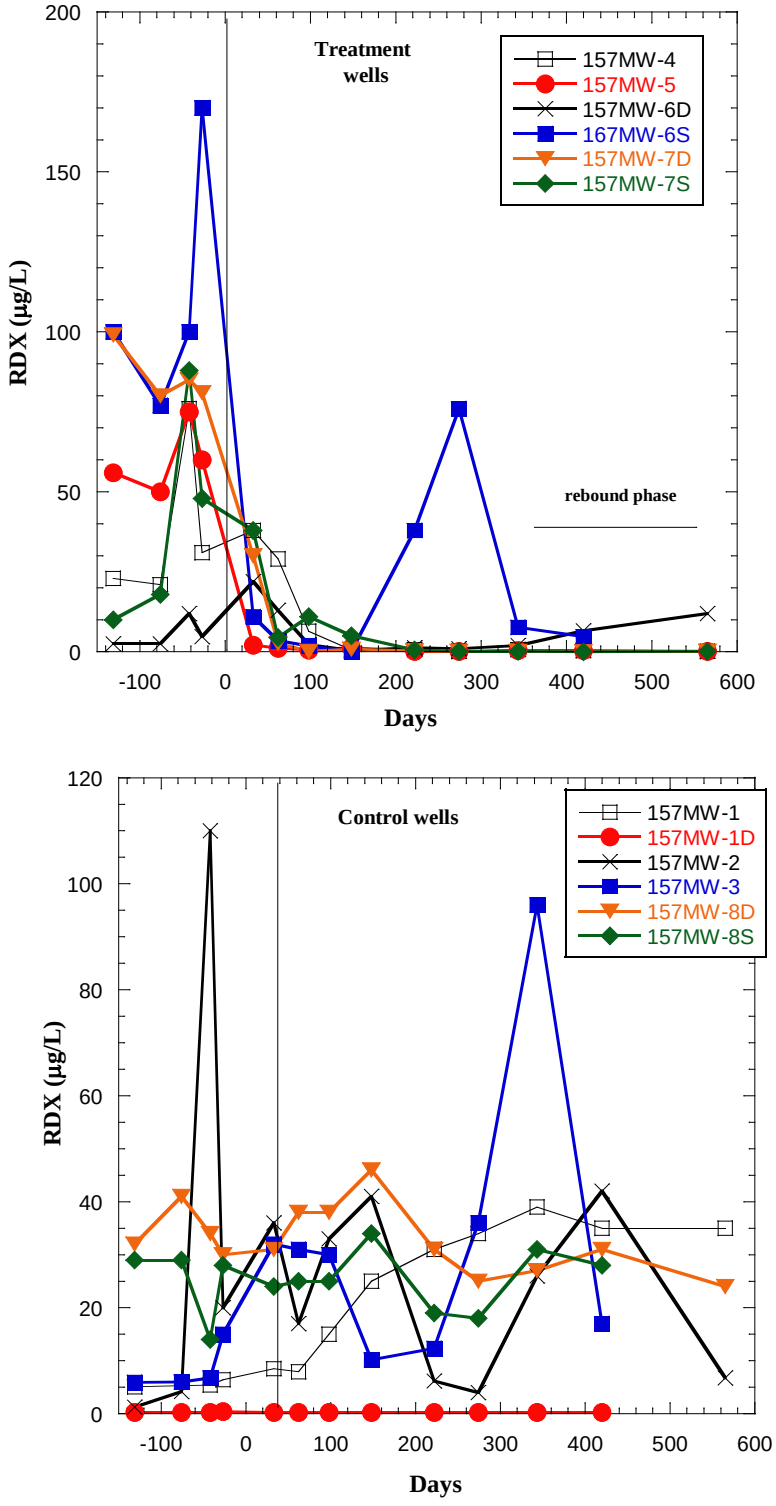
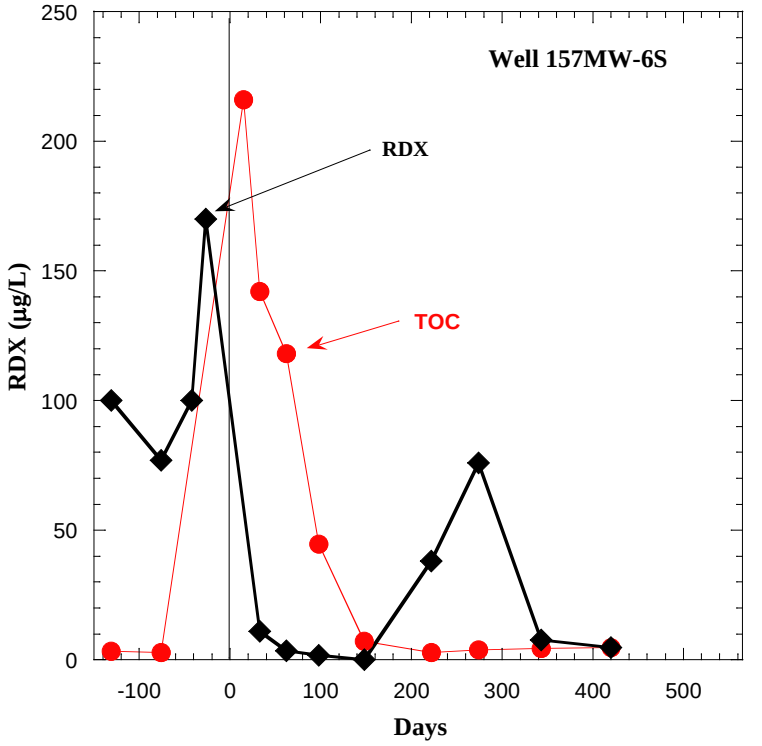


Figure 5.35. Concentrations of RDX in treatment wells (top panel) and control wells (bottom panel) in treatment zone monitoring wells.



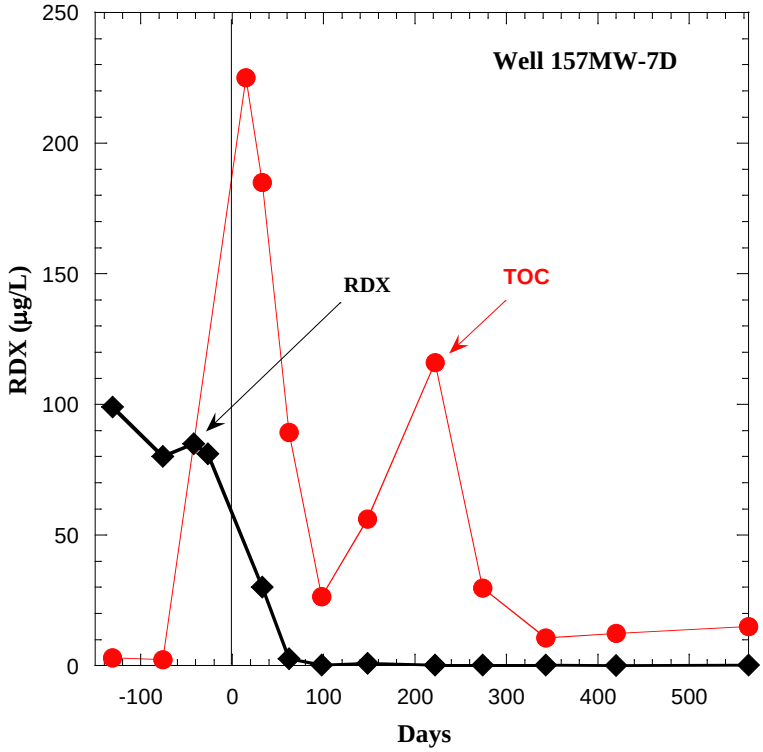


Figure 5.36. Comparison of TOC and RDX concentrations in wells 157MW-6S and 157MW-7D.

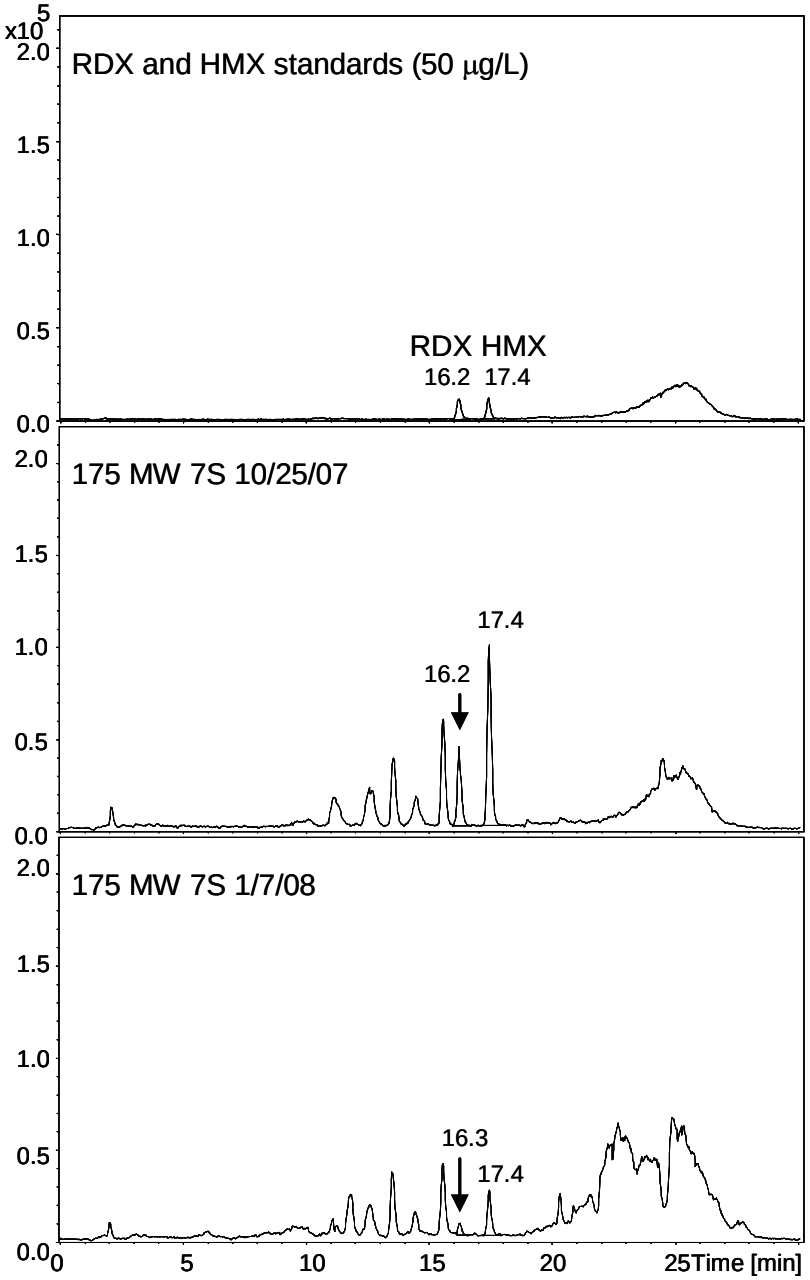


Figure 5.37. Ion chromatograms (EIC, at m/z 113) of RDX (16.2 min) and HMX (17.4 min) standards (50 μg/L), and samples from TZMW 175MW-7S obtained by LC-MS using electrospray negative ionization mode.

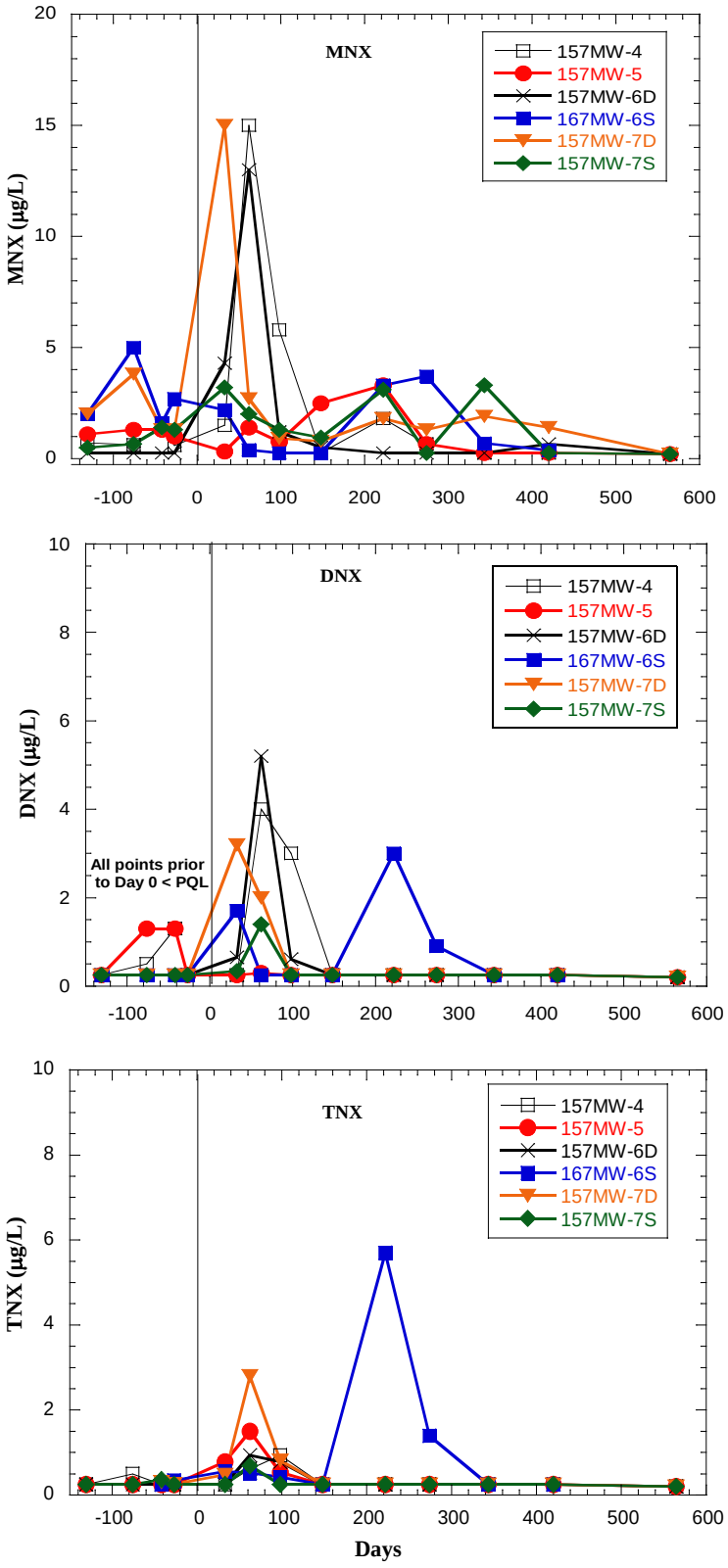


Figure 5.38. Concentrations of MNX (top panel), DNX (middle panel), and TNX (bottom panel) in treatment zone monitoring wells.

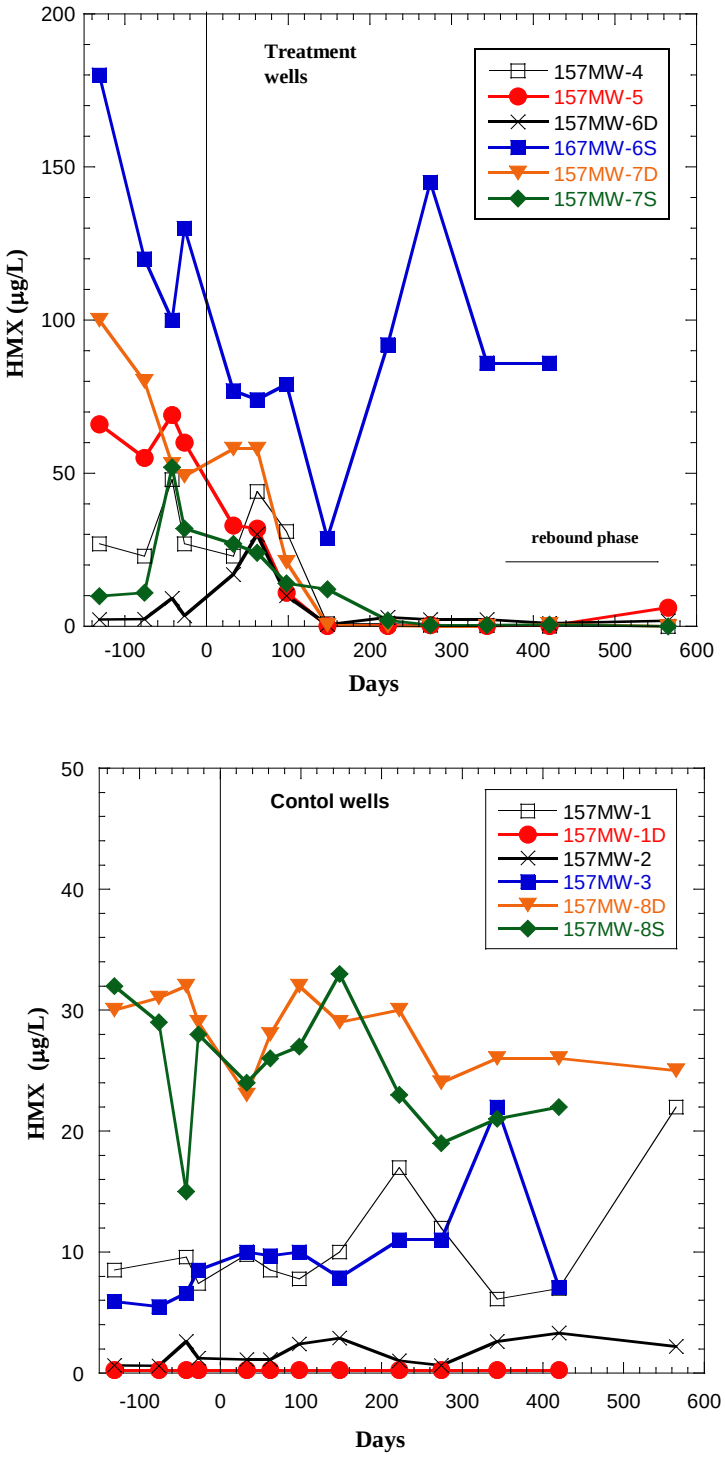


Figure 5.39. Concentrations of HMX in treatment wells (top panel) and control wells (bottom panel) in treatment zone monitoring wells.

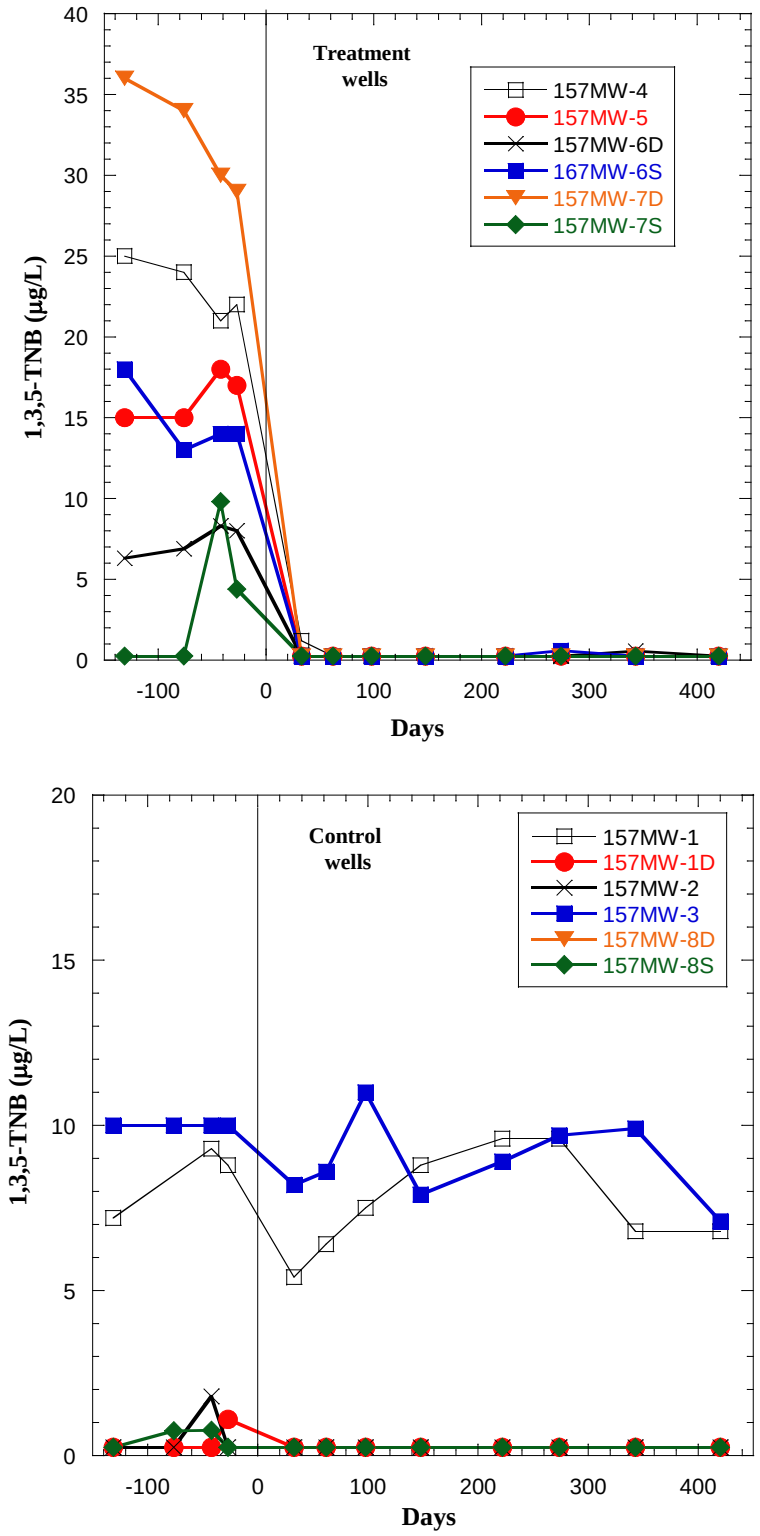


Figure 5.40. Concentrations of 1,3,5-trinitrobenzene in treatment wells (top panel) and control wells (bottom panel).

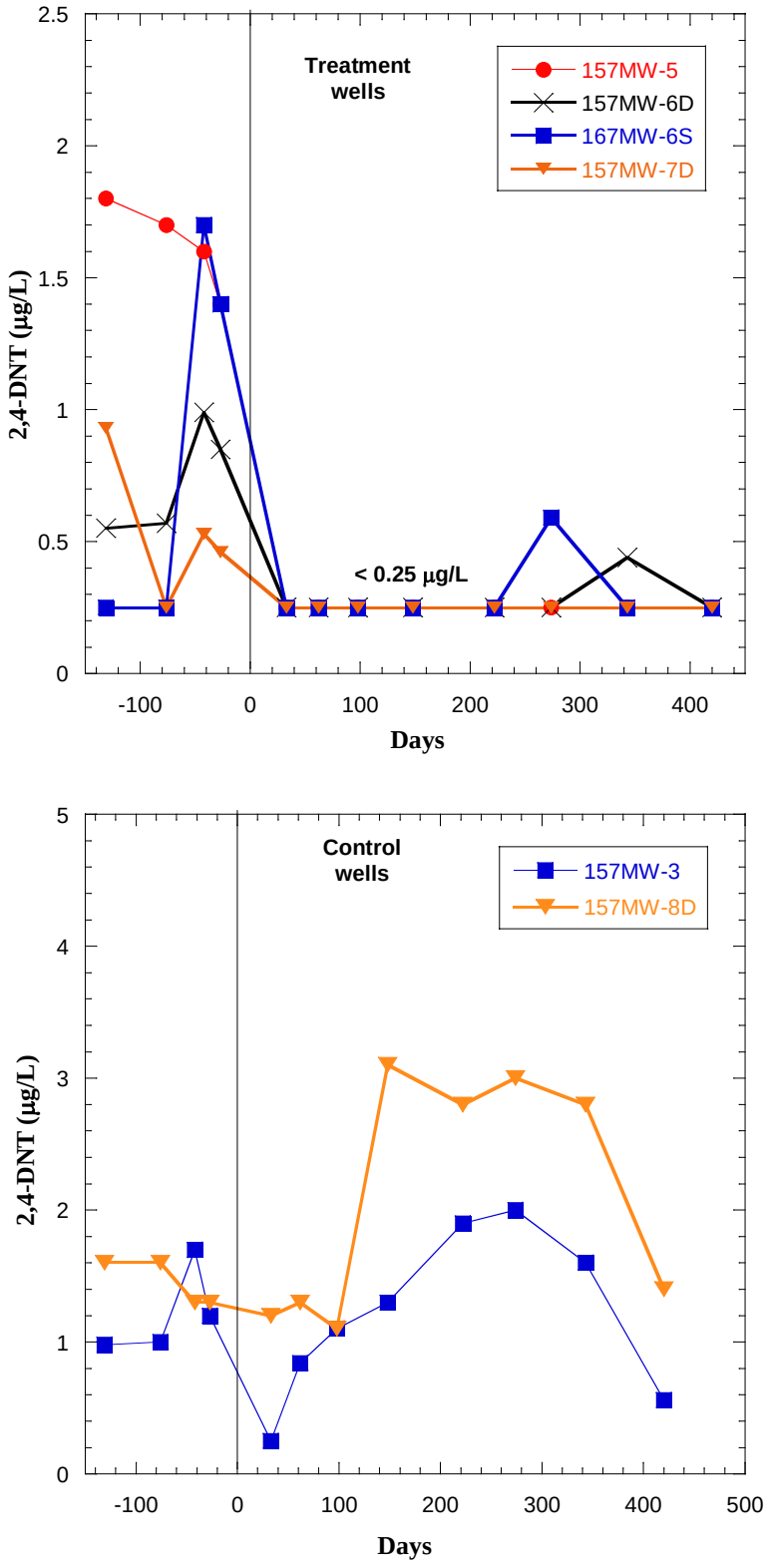


Figure 5.41. Concentrations of 2,4-dinitrotoluene in select treatment wells (top panel) and control wells (bottom panel). Values in all other wells were near or below detection throughout the demonstration.

Table 5.16. RDX Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	5.1	<0.25	1.3	5.9	23	56	2.5	100	99	10	32	29
03/15/07	-76	11	110	ND[1]	<0.25	4.2	6.0	21	50	2.5	77	80	18	41	29
04/18/07	-42	ND[1]	ND[1]	5.4	<0.25	110	6.8	76	75	12	100	85	88	34	14
5/3/2007	-27	3.8	110	6.4	0.41	20	15	31	60	4.7	170	81	48	30	28
7/2/2007	33	37	99	8.5	<0.25	36	32	38	2.1	22	11	30	38	31	24
7/31/2007	62	12	48	7.9	<0.25	17	31	29	1.2	13	3.5	2.6	4.5	38	25
9/5/2007	98	18	14	15	<0.25	33	30	6.4	0.64	2.3	1.8	0.25	11	38	25
10/25/2007	148	69	41	25	<0.25	41	10^	0.52^	1.3^	0.36^	<0.1^	0.86^	5.0^	46	34
1/7/2008	222	23	40	31	<0.25	6.2	12^	0.69^	0.22^	1.2^	38	0.31^	0.58^	31	19
2/28/2008	274	26	27	34^	<0.25	4.0	36	<0.2^	<0.2^	1.0^	76^	<0.2^	<0.2^	25	18
5/7/2008	343	18	20	39^	<0.25	26	96	0.79	0.45	2.0^	7.7^	<0.2^	<0.2^	27	31
7/23/2008	420	ND[1]	ND[1]	35	<0.25	42	17	0.44	0.40	6.6^	4.7^	<0.1^	<0.1^	31	28
12/15/2008	565	ND[1]	ND[1]	35	ND[1]	6.8	ND[1]	<0.2	<0.2	12	ND[1]	<0.2	<0.2	24	ND[1]

[1]ND, Not Determined

^Data obtained via LC/MS analysis

Table 5.17. MNX Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	0.25	<0.25	<0.25	<0.25	0.71	<1.1	<0.25	<2	<2	0.49	<1	1.1
03/15/07	-76	0.28	<3.8	ND[1]	<0.25	<0.25	<0.25	0.62	<1.3	<0.25	<5	<3.8	0.66	<1.3	1.1
04/18/07	-42	ND[1]	ND[1]	<0.25	<0.25	5.0	<0.25	1.5	<1.3	<0.25	1.6	1.3	1.4	<1.3	0.57
5/3/2007	-27	<0.25	2.8	<0.25	<0.25	0.82	<0.25	0.59	1.0	<0.25	2.7	1.3	1.3	0.92	0.93
7/2/2007	33	5.8	3.5	<0.25	<0.25	1.7	0.36	1.5	0.32	4.3	2.2	15	3.2	0.77	0.87
7/31/2007	62	3.0	2.5	<0.25	<0.25	0.69	0.28	15	1.4	13	0.39	2.7	2.0	0.83	0.78
9/5/2007	98	2.0	1.8	0.36	<0.25	1.1	0.31	5.8	0.76	1.2	<0.25	0.92	1.3	0.81	0.80
10/25/2007	148	<0.25	1.6	0.39	<0.25	1.5	<0.25	<0.25	2.5	0.5	<0.25	0.77	0.94	0.97	1.6
1/7/2008	222	3.1	2.9	0.70	<0.25	<0.25	0.35	1.8	3.3	<0.25	3.3	1.8	3.1	1.1	0.59
2/28/2008	274	2.4	<0.25	0.46	<0.25	<0.25	0.81	0.66	0.66	<0.25	3.7	1.3	<0.25	0.68	0.56
5/7/2008	343	0.8	<0.25	0.62	<0.25	0.66	2.2	<0.25	<0.25	0.26	0.69	1.9	3.3	0.67	0.88
7/23/2008	420	ND[1]	<0.25	0.60	<0.25	1.1	0.31	<0.25	<0.25	0.66	0.37	1.4	<0.25	0.69	0.84
12/15/2008	565	ND[1]	ND[1]	0.50	ND[1]	<0.2	ND[1]	<0.2	<0.2	<0.2	ND[1]	<0.2	<0.2	0.50	ND[1]

[1]ND, Not Determined

Table 5.18. DNX Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1	<5
03/15/07	-76	<0.25	<3.8	ND[1]	<0.25	<0.25	<0.25	<0.5	<1.3	<0.25	<5	<3.8	<0.25	<1.3	<0.75
04/18/07	-42	ND[1]	ND[1]	<0.25	<0.25	<1.8	<0.25	<1.3	<1.3	<0.25	<0.25	<0.25	<0.25	<1.3	<0.25
5/3/2007	-27	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
7/2/2007	33	**1.2**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.65**	**1.7**	**3.2**	**0.34**	<0.25	<0.25
7/31/2007	62	**1.7**	**0.36**	<0.25	<0.25	<0.25	<0.25	**4.0**	**0.30**	**5.2**	<0.25	**2.0**	**1.4**	<0.25	<0.25
9/5/2007	98	**0.69**	**0.45**	<0.25	<0.25	<0.25	<0.25	**3.0**	<0.25	**0.61**	<0.25	<0.25	**0.25**	<0.25	<0.25
10/25/2007	148	<0.25	**0.92**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
1/7/2008	222	**0.94**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	3.0	<0.25	<0.25	<0.25	<0.25
2/28/2008	274	**0.54**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	0.9	<0.25	<0.25	<0.25	<0.25
5/7/2008	343	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
7/23/2008	420	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
12/15/2008	565	ND[1]	ND[1]	<0.2	ND[1]	<0.2	ND[1]	<0.2	<0.2	<0.2	ND[1]	<0.2	<0.2	<0.2	ND[1]

[1]ND, Not Determined

Table 5.19. TNX Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are data from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<4.5	<3	<0.25	<1	<0.25
03/15/07	-76	<0.25	<3.8	ND[1]	<0.25	<0.25	<0.25	<0.5	<1.3	<0.25	<5	<3.8	<0.25	<1.3	<0.75
04/18/07	-42	ND[1]	ND[1]	<0.25	<0.25	<1.8	<0.25	<1.3	<1.3	<0.25	**0.25**	**0.31**	**0.37**	<1.3	<0.25
5/3/2007	-27	<0.25	2.8	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.35**	**0.26**	<0.25	**0.31**	<0.25
7/2/2007	33	**0.86**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.78**	<0.25	**0.56**	**0.48**	<0.25	**0.26**	<0.25
7/31/2007	62	**1.1**	**0.28**	<0.25	<0.25	<0.25	<0.25	**0.61**	**1.5**	**0.94**	**0.53**	**2.8**	**0.69**	<0.25	<0.25
9/5/2007	98	**0.63**	**0.26**	<0.25	<0.25	<0.25	<0.25	**0.94**	**0.54**	**0.79**	**0.42**	**0.81**	<0.25	**0.29**	<0.25
10/25/2007	148	<0.25	**1.5**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
1/7/2008	222	**1.1**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**5.7**	<0.25	<0.25	**0.27**	<0.25
2/28/2008	274	**0.26**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**1.4**	<0.25	<0.25	<0.25	<0.25
5/7/2008	343	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
7/23/2008	420	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
12/15/2008	565	ND[1]	ND[1]	<0.2	ND[1]	<0.2	ND[1]	<0.2	<0.2	<0.2	ND[1]	<0.2	<0.2	<0.2	ND[1]

[1]ND, Not Determined

[#]Results reported are from the phenyl hexyl confirmation column for Method 8330 because TNX and 2,6-Diamino-4-nitrotoluene were reported to co-elute on the LC-18 (i.e., reporting) column.

Table 5.20. HMX Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are data from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	8.5	<0.25	0.62	5.9	27	66	2.2	180	100	9.9	30	32
03/15/07	-76	17	58	ND[1]	<0.25	0.59	5.5	23	55	2.4	120	80	11	31	29
04/18/07	-42	ND[1]	ND[1]	9.6	<0.25	2.6	6.6	48	69	9.2	100	53	52	32	15
5/3/2007	-27	0.42	66	7.4	<0.25	1.2	8.5	27	60	3.5	130	49	32	29	28
7/2/2007	33	32	54	9.8	<0.25	1.1	10	23	33	17	77	58	27	23	24
7/31/2007	62	22	42	8.5	<0.25	1.1	9.7	44	32	30	74	58	24	28	26
9/5/2007	98	14	34	7.8	<0.25	2.4	10	31	11	10	79	21	14	32	27
10/25/2007	148	4.6	56	10	<0.25	2.9	7.9^	0.88^	<0.12^	0.52^	29^	0.44^	12^	29	33
1/7/2008	222	18	4.4	17	<0.25	1.0	10^	1.0^	<0.12^	2.9^	92	<0.12^	2.0^	30	23
2/28/2008	274	18	0.35	12^	<0.25	0.64	11	<0.4^	<0.4^	2.3^	145^	<0.4^	<0.4^	24	19
5/7/2008	343	15	1.2	6.1^	<0.25	2.6	22	0.28	<0.25	2.3^	86^	<0.4^	<0.4^	26	21
7/23/2008	420	ND[1]	ND[1]	7.0	<0.25	3.3	7.1	<0.25	<0.25	1.0	86	0.7	0.62	26	22
12/15/2008	565	ND[1]	ND[1]	22	ND[1]	2.2	ND[1]	<0.1	6.2	1.8	ND[1]	<0.1	<0.1	25	ND[1]

[1]ND, Not Determined

^Data obtained via LC/MS analysis

Table 5.21. 1,3,5-Trinitrobenzene Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells**.**

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	7.2	<0.25	<0.25	10	25	15	6.3	18	36	<0.25	62	<0.25
03/15/07	-76	4.4	20	ND[1]	<0.25	<0.25	10	24	15	6.9	13	34	<0.25	69	<0.75
04/18/07	-42	ND[1]	ND[1]	9.3	<0.25	<1.8	10	21	18	8.3	14	30	9.8	72	0.76
5/3/2007	-27	<0.25	13	8.8	1.1	<0.25	10	22	17	8.0	14	29	4.4	68	<0.25
7/2/2007	33	<0.25	3.4	5.4	<0.25	<0.25	8.2	1.2	<0.25	<0.25	<0.25	<0.25	<0.25	57	<0.25
7/31/2007	62	<0.25	0.74	6.4	<0.25	<0.25	8.6	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	61	<0.25
9/5/2007	98	<0.25	<0.25	7.5	<0.25	<0.25	11	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	69	<0.25
10/25/2007	148	<0.25	<0.25	8.8	<0.25	<0.25	7.9	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	58	<0.25
1/7/2008	222	<0.25	<0.25	9.6	<0.25	<0.25	8.9	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	69	<0.25
2/28/2008	274	<0.25	<0.25	9.6	<0.25	<0.25	9.7	<0.25	<0.25	<0.25	0.59	<0.25	<0.25	54	<0.25
5/7/2008	343	<0.25	<0.25	6.8	<0.25	<0.25	9.9	<0.25	<0.25	0.56	<0.25	<0.25	<0.25	68	<0.25
7/23/2008	420	<0.25	<0.25	6.8	<0.25	<0.25	7.1	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	63	<0.25

[1]ND, Not Determined

Table 5.22. 2,4-Dinitrotoluene Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.25	<0.25	<0.25	**0.98**	<0.25	**1.8**	**0.55**	<2.6	**0.93**	<0.25	**1.6**	<0.25
03/15/07	-76	<0.25	<3.8	ND[1]	<0.25	<0.25	**1.0**	<0.5	**1.7**	**0.57**	<5	<3.8	<0.25	**1.6**	<0.75
04/18/07	-42	ND[1]	ND[1]	<0.25	<0.25	<1.8	**1.7**	<1.3	**1.6**	**0.99**	**1.7**	**0.53**	**0.58**	**1.3**	<0.25
5/3/2007	-27	<0.25	<0.25	<0.25	<0.25	<0.25	**1.2**	<0.25	**1.4**	**0.85**	**1.4**	**0.46**	<0.25	**1.3**	<0.25
7/2/2007	33	**5.8**	**0.55**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**1.2**	<0.25
7/31/2007	62	<0.25	<0.25	<0.25	<0.25	<0.25	**0.84**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**1.3**	<0.25
9/5/2007	98	<0.25	<0.25	<0.25	<0.25	<0.25	**1.1**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**1.1**	<0.25
10/25/2007	148	<0.25	<0.25	<0.25	<0.25	<0.25	**1.3**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**3.1**	<0.25
1/7/2008	222	<0.25	<0.25	<0.25	<0.25	<0.25	**1.9**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**2.8**	<0.25
2/28/2008	274	<0.25	<0.25	<0.25	<0.25	<0.25	**2.0**	<0.25	<0.25	<0.25	**0.74**	<0.25	<0.25	**3.0**	<0.25
5/7/2008	343	<0.25	<0.25	<0.25	<0.25	<0.25	**1.6**	<0.25	<0.25	**0.44**	<0.25	<0.25	**0.47**	**2.8**	<0.25
7/23/2008	420	<0.25	<0.25	<0.25	<0.25	<0.25	**0.56**	<0.25	<0.25	<0.25	<0.25	<0.25	**0.28**	**1.4**	<0.25

[1]ND, Not Determined

Table 5.23. 2,6-Dinitrotoluene Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.25	<0.25	<0.25	**0.98**	<0.25	**1.8**	**0.55**	<2.6	**0.93**	<0.25	**1.6**	<0.25
03/15/07	-76	<0.25	<3.8	ND[1]	<0.25	<0.25	**1.0**	<0.5	**1.7**	**0.57**	<5	<3.8	<0.25	**1.6**	<0.75
04/18/07	-42	ND[1]	ND[1]	<0.25	<0.25	<1.8	**1.7**	<1.3	**1.6**	**0.99**	**1.7**	**0.53**	**0.58**	**1.3**	<0.25
5/3/2007	-27	<0.25	<0.25	<0.25	<0.25	<0.25	**1.2**	<0.25	**1.4**	**0.85**	**1.4**	**0.46**	<0.25	**1.3**	<0.25
7/2/2007	33	**5.8**	**0.55**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**1.2**	<0.25
7/31/2007	62	<0.25	<0.25	<0.25	<0.25	<0.25	**0.84**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**1.3**	<0.25
9/5/2007	98	<0.25	<0.25	<0.25	<0.25	<0.25	**1.1**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**1.1**	<0.25
10/25/2007	148	<0.25	<0.25	<0.25	<0.25	<0.25	**1.3**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**3.1**	<0.25
1/7/2008	222	<0.25	<0.25	<0.25	<0.25	<0.25	**1.9**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**2.8**	<0.25
2/28/2008	274	<0.25	<0.25	<0.25	<0.25	<0.25	**2.0**	<0.25	<0.25	<0.25	**0.74**	<0.25	<0.25	**3.0**	<0.25
5/7/2008	343	<0.25	<0.25	<0.25	<0.25	<0.25	**1.6**	<0.25	<0.25	**0.44**	<0.25	<0.25	**0.47**	**2.8**	<0.25
7/23/2008	420	<0.25	<0.25	<0.25	<0.25	<0.25	**0.56**	<0.25	<0.25	<0.25	<0.25	<0.25	**0.28**	**1.4**	<0.25

[1]ND, Not Determined

Table 5.24. 1,3-Dinitrobenzene Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.25	<0.25	<0.25	**0.29**	<0.25	<0.6	<0.25	<0.7	<0.25	<0.25	**0.37**	<0.25
03/15/07	-76	<0.25	<3.8	ND[1]	<0.25	<0.25	<0.25	<0.5	<1.3	<0.25	<5	<3.8	<0.25	<1.3	<0.75
04/18/07	-42	ND[1]	ND[1]	<0.25	<0.25	<1.8	**0.38**	<1.3	<1.3	**0.37**	**0.73**	<0.25	**0.26**	<1.3	<0.25
5/3/2007	-27	<0.25	<0.25	<0.25	<0.25	<0.25	**0.29**	<0.25	**0.56**	**0.33**	**0.70**	<0.25	<0.25	**0.37**	<0.25
7/2/2007	33	**0.62**	<0.25	**0.34**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.50**	<0.25
7/31/2007	62	<0.25	**0.38**	**0.35**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.54**	<0.25
9/5/2007	98	<0.25	<0.25	<0.25	<0.25	<0.25	**0.31**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.45**	<0.25
10/25/2007	148	<0.25	<0.25	**0.49**	<0.25	<0.25	**0.28**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.46**	<0.25
1/7/2008	222	<0.25	<0.25	**0.26**	<0.25	<0.25	**0.34**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.45**	<0.25
2/28/2008	274	<0.25	<0.25	<0.25	<0.25	<0.25	**0.46**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.35**	<0.25
5/7/2008	343	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**74**	**0.42**	<0.25
7/23/2008	420	<0.25	<0.25	**0.25**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**54**	**0.44**	<0.25

[1]ND, Not Determined

Table 5.25. 2-Nitrotoluene Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<4	<3	<0.25	**1.4**	<0.25
03/15/07	-76	<0.25	<3.8	ND[1]	<0.25	<0.25	<0.25	**1.1**	<1.3	<0.25	<5	<3.8	<0.25	<1.3	<0.75
04/18/07	-42	ND[1]	ND[1]	<0.25	<0.25	<1.8	<0.25	<1.3	<1.3	<0.25	**3.8**	<0.25	**1.1**	<1.3	<0.25
5/3/2007	-27	**0.45**	<0.25	<0.25	<0.25	<0.25	<0.25	**1.1**	**2.5**	<0.25	**4.9**	**2.5**	<0.25	**1.5**	<0.25
7/2/2007	33	**1.4**	**1.7**	<0.25	<0.25	<0.25	<0.25	**5.1**	<0.25	<0.25	**4.3**	<0.25	**0.38**	**1.4**	<0.25
7/31/2007	62	<0.25	**0.42**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**1.3**	<0.25
9/5/2007	98	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**1.3**	<0.25
10/25/2007	148	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
1/7/2008	222	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
2/28/2008	274	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
5/7/2008	343	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**1.4**	<0.25
7/23/2008	420	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**1.2**	<0.25

[1]ND, Not Determined

Table 5.26. 3-Nitrotoluene Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1	<0.25
03/15/07	-76	<0.25	<3.8	ND[1]	<0.25	<0.25	<0.25	<0.5	<1.3	<0.25	<5	<3.8	<0.25	<1.3	<0.75
04/18/07	-42	ND[1]	ND[1]	<0.25	<0.25	<1.8	<0.25	<1.3	<1.3	<0.25	<0.25	<0.25	<0.25	<1.3	<0.25
5/3/2007	-27	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
7/2/2007	33	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
7/31/2007	62	**0.55**	**0.38**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
9/5/2007	98	**0.49**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**1.5**	<0.25	<0.25	<0.25	<0.25
10/25/2007	148	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
1/7/2008	222	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
2/28/2008	274	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
5/7/2008	343	<0.25	<0.25	<0.25	<0.25	<0.25	**0.30**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
7/23/2008	420	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25

[1]ND, Not Determined

Table 5.27. 4-Nitrotoluene Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1	<5
03/15/07	-76	<0.25	<3.8	ND[1]	<0.25	<0.25	<0.25	<0.5	<1.3	<0.25	<5	<3.8	<0.25	<1.3	<0.75
04/18/07	-42	ND[1]	ND[1]	<0.25	<0.25	<1.8	<0.25	<1.3	<1.3	<0.25	<0.25	<0.25	<0.25	<1.3	<0.25
5/3/2007	-27	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
7/2/2007	33	<0.25	**1.5**	<0.25	<0.25	<0.25	<0.25	**2.4**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
7/31/2007	62	<0.25	**0.35**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
9/5/2007	98	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
10/25/2007	148	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
1/7/2008	222	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
2/28/2008	274	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
5/7/2008	343	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.27**	<0.25	<0.25
7/23/2008	420	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.29**	<0.25	<0.25

[1]ND, Not Determined

Table 5.28. Pentaerythritol tetranitrate (PETN) Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<10	<10	<10	**15**	<19	**31**	<10	<13	<30	<10	<40	<10
03/15/07	-76	**18**	<150	ND[1]	<10	<10	**27**	<20	**58**	**11**	<200	<150	<10	<50	<30
04/18/07	-42	ND[1]	ND[1]	<10	<10	<10	<10	<50	<50	<10	**15**	<10	<10	<50	<10
5/3/2007	-27	<10	**13**	<10	<10	<10	<10	<10	<10	<10	**34**	<10	<10	<10	<10
7/2/2007	33	<10	**14**	<10	<10	<10	**13**	<10	<10	<10	<10	<10	<10	**63**	<10
7/31/2007	62	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
9/5/2007	98	<10	**12**	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
10/25/2007	148	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
1/7/2008	222	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
2/28/2008	274	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
5/7/2008	343	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
7/23/2008	420	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

[1]ND, Not Determined

Table 5.29. 2,4,6-Trinitrophenol (Picric Acid) Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.25	<0.25	<0.25	<0.25	**0.32**	<0.25	<0.25	**0.41**	**0.55**	<0.25	<1	<0.25
03/15/07	-76	<0.25	<3.8	ND[1]	<0.25	<0.25	<0.25	<0.5	<1.3	<0.25	<5	<3.8	<0.25	<1.3	<0.75
04/18/07	-42	ND[1]	ND[1]	<0.25	<0.25	<1.8	<0.25	<1.3	<1.3	<0.25	<0.25	<0.25	<0.25	<1.3	<0.25
5/3/2007	-27	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.25**	**0.41**	<0.25	**0.69**	**0.28**	<0.25	**0.25**	<0.25
7/2/2007	33	**0.34**	<0.25	<0.25	<0.25	<0.25	<0.25	**0.45**	<0.25	<0.25	<0.25	<0.25	<0.25	**0.35**	<0.25
7/31/2007	62	**0.27**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.60**	<0.25
9/5/2007	98	**0.26**	<0.25	<0.25	<0.25	<0.25	**0.28**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.72**	<0.25
10/25/2007	148	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.36**	<0.25
1/7/2008	222	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
2/28/2008	274	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
5/7/2008	343	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
7/23/2008	420	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.77**	<0.25

[1]ND, Not Determined

Table 5.30. 2,4,6-Trinitrophenylmethylnitramine (Tetryl) Concentrations in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1	<0.25
03/15/07	-76	<0.25	<3.8	ND[1]	<0.25	<0.25	<0.25	<0.5	<1.3	<0.25	<5	<3.8	<0.25	<1.3	<0.75
04/18/07	-42	ND[1]	ND[1]	<0.25	<0.25	<1.8	<0.25	<1.3	<1.3	<0.25	<0.25	<0.25	<0.25	<1.3	<0.25
5/3/2007	-27	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
7/2/2007	33	**0.41**	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
7/31/2007	62	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**0.38**	<0.25	<0.25	<0.25	<0.25	<0.25
9/5/2007	98	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
10/25/2007	148	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
1/7/2008	222	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
2/28/2008	274	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	**230**	<0.25	<0.25
5/7/2008	343	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
7/23/2008	420	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25

[1]ND, Not Determined

5.6.3 Field Parameters

5.6.3.1 Oxidation-Reduction Potential (ORP)

A rapid decrease in oxidation-reduction potential (ORP) as a result of whey injection and corresponding microbial activity was observed in all of the TZMWs **(Figure 5.42** and **Table 5.31).** The ORP values in all wells except the deep bedrock well (157MW-1D) were positive and generally greater than + 200 mV prior to cosubstrate injection. After whey injection, values declined to < -100 mV in all TMZWs, and values < -400 mV were observed transiently in some of the wells. No significant decline in ORP was observed in the CZMWs. During the rebound phase, the ORP values gradually increased in upgradient TZMWs 157MW-6S and 157MW-6D, consistent with the low TOC values in these wells, but they remained < -100 mV in all of the downgradient TZMWs at Day 565, more than one year after the final injection of whey. The data illustrate the potential longevity of treatment with this approach.

5.6.3.2 pH

The pH in the TZMWs increased somewhat after whey injection; while the pH in the CZMWs remained reasonably steady **(Figure 5.43** and **Table 5.32).** The pre-amendment pH values ranged from ~ 5.2 to 6.4 (with the exception of the bedrock well 157MW-1D which has a pH near 7.4). On Day 148 after the initial whey injection, the pH in the TMZWs was very consistent, and ranged from 6.5 to 6.7, with all wells showing a pH increase of at least 0.5 S.U. Given the biodegradation activity and the presumed production of fatty acids during whey fermentation, the data suggest that the whey provided some buffering capacity to the groundwater. The pH declined to pre-amendment levels in wells 157MW-6S and 157MW-6D by the end of the rebound phase, but remained elevated in the other TZMWs.

5.6.3.3 Dissolved Oxygen

The dissolved oxygen (DO) in the TZMWs ranged from ~ 1 to 3 mg/L (with the exception of the bedrock well 157MW-1D which has a DO near 0.5 mg/L) prior to whey addition **(Table 5.33)**. As expected, given the large quantities of whey added, the DO in all of the TZMWs declined to generally < 0.5 mg/L during the active treatment phase. DO concentrations in the CZMWs remained near their pre-demonstration concentrations.

5.6.3.4 Temperature

The groundwater temperature during the demonstration ranged from ~ 9 to 13^{o}C depending on the time of the year **(Table 5.34)**. There were no appreciable differences apparent between the TZMWs and the CZMWs during the course of the study.

5.6.3.5 Depth to Water

The depth to groundwater is presents in **Figure 5.44** and **Table 5.35**. The most noticeable change in water table elevation occurred between October 25, 2007 (Day 148) and January 07 2008 (Day 222). During this time, heavy rainfall caused the water table to rise by nearly 2 ft throughout the demonstration plot. This may also have contributed to the increased concentrations of RDX in well 157MW-6S during this period due to flushing of RDX from the vadose zone.

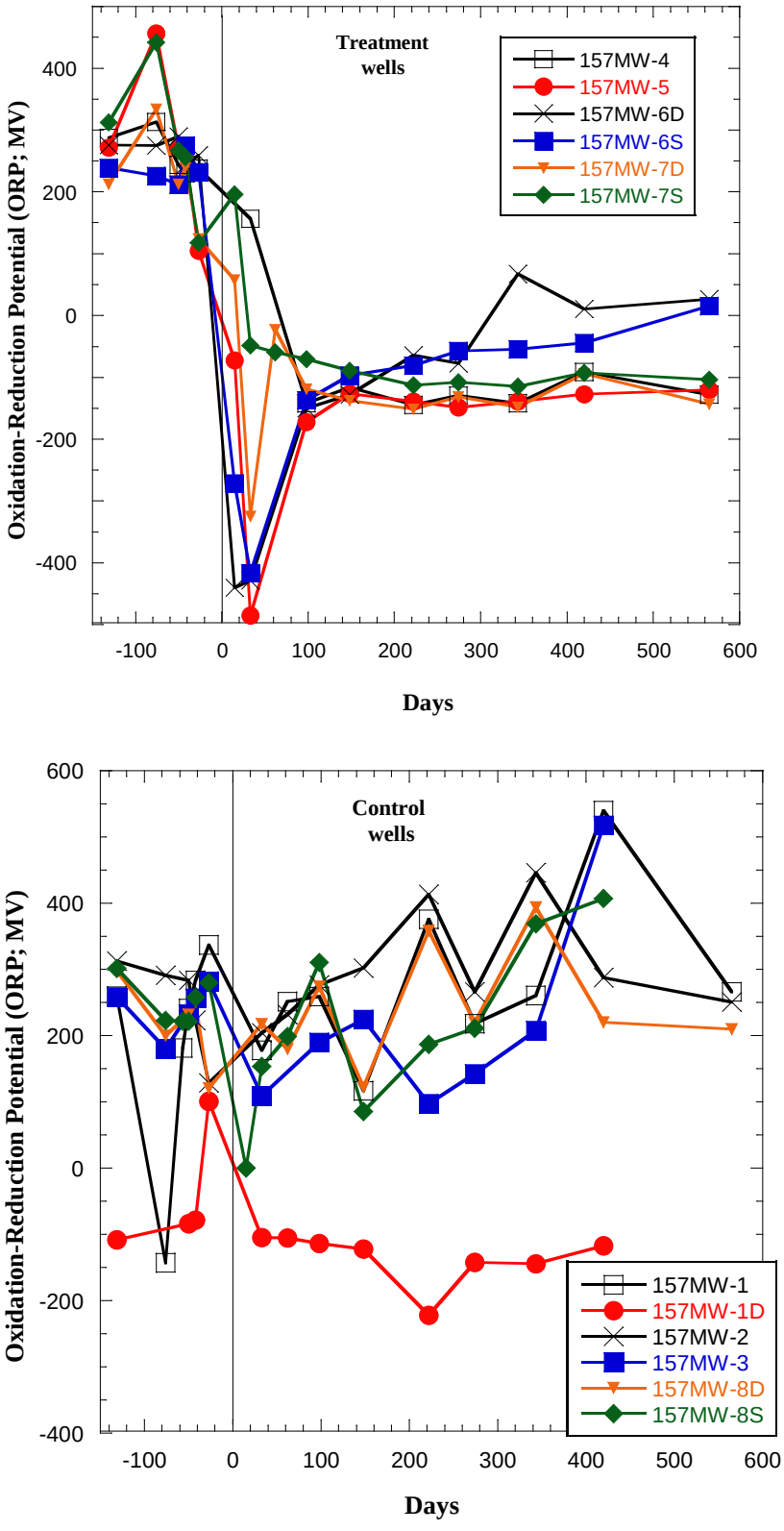


Figure 5.42. Oxidation-reduction potential (ORP) in treatment wells (top panel) and control wells (bottom panel) during the course of the demonstration.

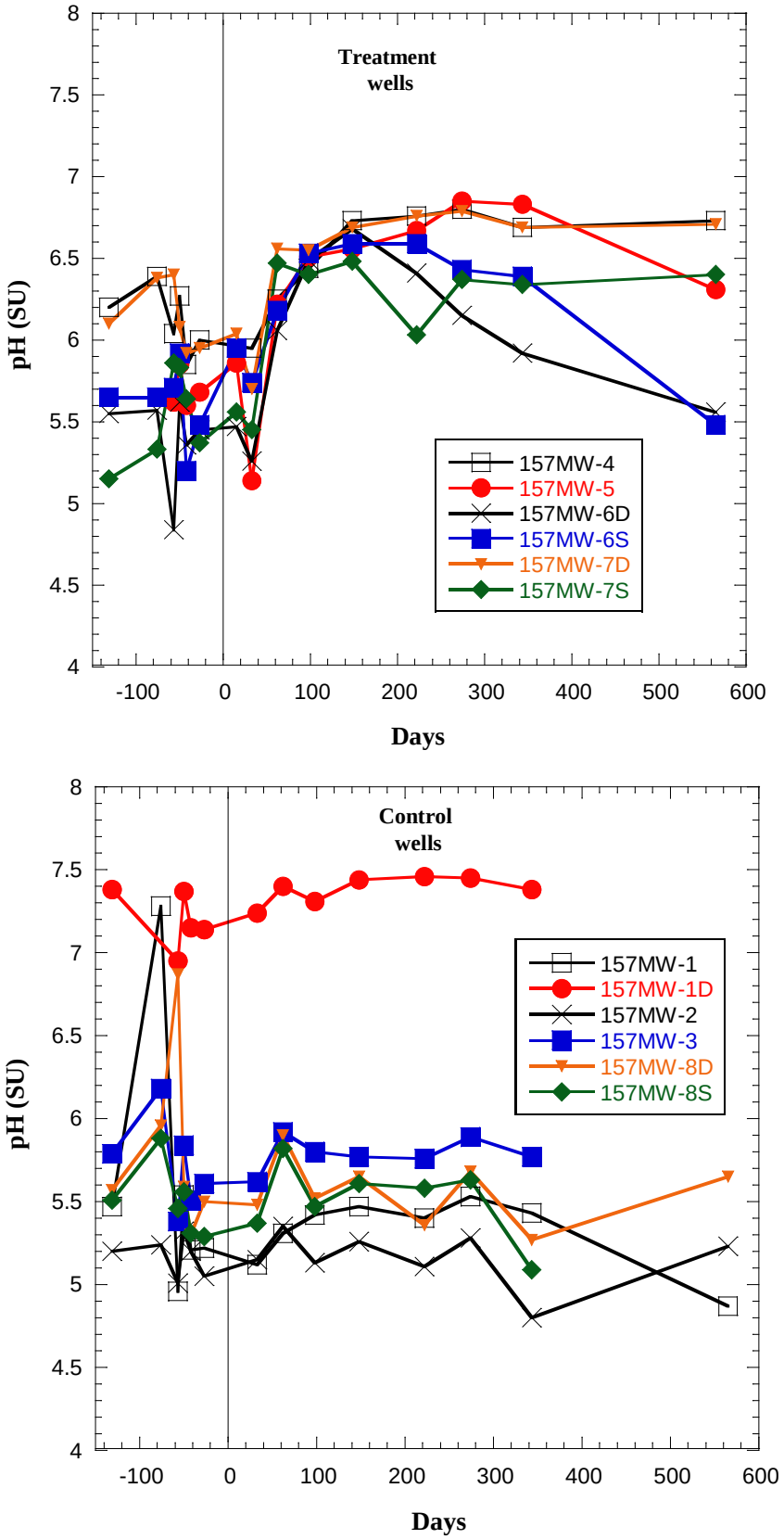


Figure 5.43. pH in treatment wells (top panel) and control wells (bottom panel) during the course of the demonstration.

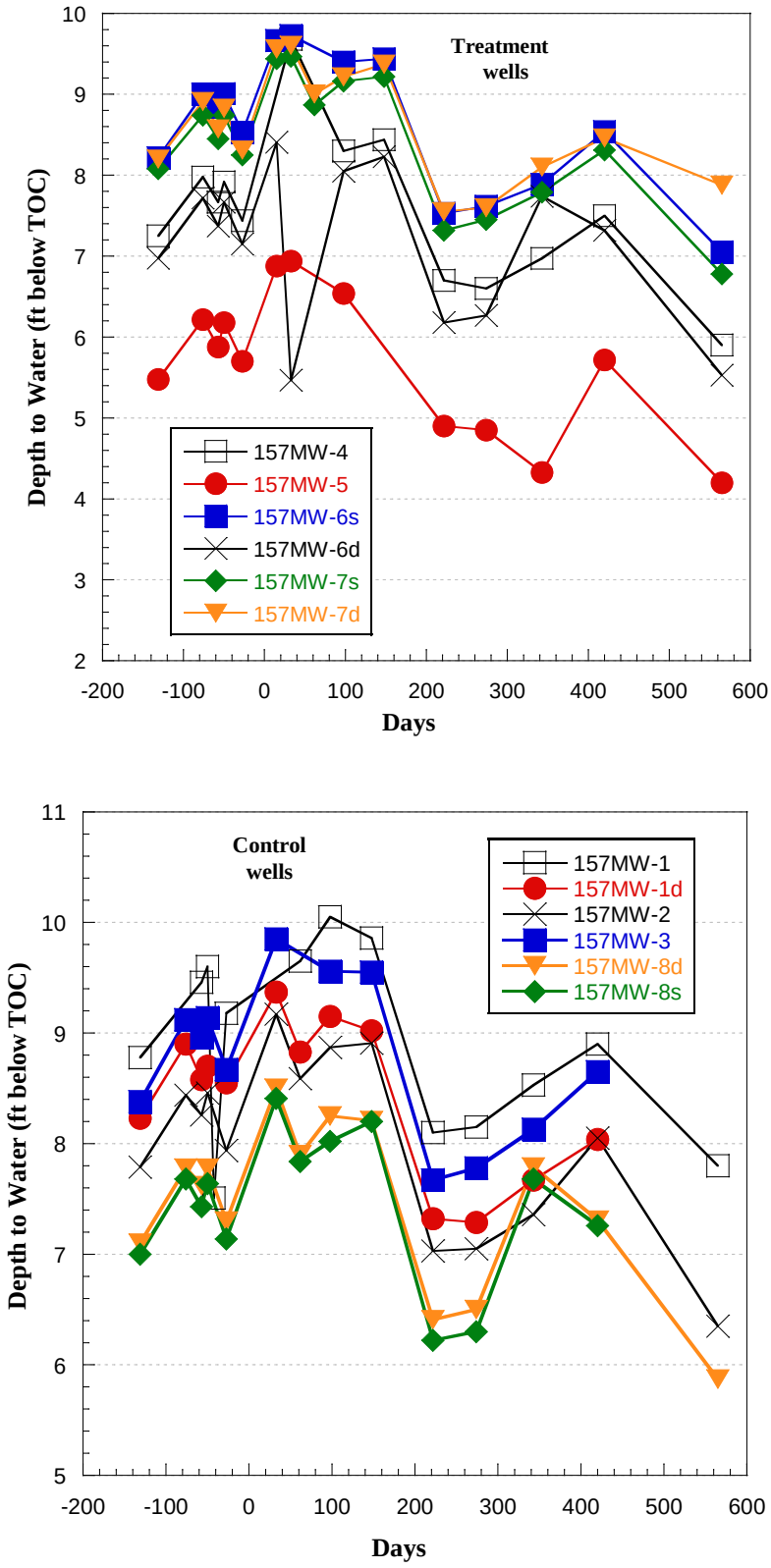


Figure 5.44. Depth to water in treatment wells (top panel) and control wells (bottom panel) during the course of the demonstration.

Table 5.31. Oxidation-Reduction Potential (ORP) in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	260.1	-108.4	312.5	258.5	287.4	271.6	276.1	239.1	212.7	312.8	297.8	301.7
03/15/07	-76	377.9	264.8	ND[1]	-143.0	291.3	179.6	312.9	456.9	274.9	225.6	333.6	442.2	200.5	223.1
04/03/07	-57	-46.8	-60.4	181.7	-97.5	1.4	-22.0	213.3	213.5	-57.6	212.9	-205.1	-144.7	-130.8	221.8
04/10/07	-50	247.3	253.7	241.0	-84.3	283.7	232.7	244.0	271.5	289.6	212.1	213.1	267.3	232.2	221.8
04/18/07	-42	ND[1]	ND[1]	283.6	-78.1	223.0	256.5	230.2	263.6	243.7	275.1	239.7	256.7	251.2	257.5
5/3/2007	-27	135.7	149.6	336.8	100.8	128.8	282.1	237.5	104.7	259.1	232.4	124.4	117.8	121.2	279.7
6/14/2007	15	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	-72.8	-440.1	-271.2	57.6	196.0	ND[1]	ND[1]
7/2/2007	33	-204.9	39.1	177.7	-104.7	204.2	109.1	156.9	-485.4	-428.4	-417.0	-324.5	-48.2	217.2	153.7
7/31/2007	62	-21.6	156.8	251.6	-105.3	232.1	604.3	NR[2]	NR[2]	NR[2]	NR[2]	-22.3	-59.5	179.9	198.7
9/5/2007	98	1.0	-6.0	259.3	-113.8	276.7	190.1	-142.1	-172.0	-149.8	-137.3	-119.1	-70.8	274.1	310.3
10/25/2007	148	-74.5	-82.2	116.5	-121.9	302.5	224.5	-116.2	-126.6	-127.7	-96.7	-138.0	-88.8	122.4	85.6
1/7/2008	222	144.6	-55.9	376.2	-222.4	413.2	97.6	-144.9	-139.1	-64.3	-80.8	-151.7	-112.7	358.7	187.2
2/28/2008	274	-53.8	-64.0	218.0	-142.0	266.4	142.4	-129.8	-148.9	-77.5	-57.5	-131.8	-108.1	219.8	211.0
5/7/2008	343	ND[1]	ND[1]	260.5	-144.0	446.0	207.8	-141.5	-138.7	67.1	-54.7	-147.7	-114.8	394.0	368.5
7/23/2008	420	ND[1]	ND[1]	540.0	-117.6	287.8	517.7	-91.3	-127.1	10.6	-44.0	-94.0	-92.9	220.1	407.2
12/15/2008	565	ND[1]	ND[1]	265.8	ND[1]	250.8	ND[1]	-128.3	-120.4	26.8	15.2	-143.1	-103.5	209.8	ND[1]

[1]ND, Not Determined

[2]NR, Not Reported. Data not reported due to a malfunction of the YSI field meter

Table 5.32. pH in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	5.47	7.38	5.20	5.79	6.20	5.65	5.55	5.65	6.10	5.15	5.57	5.51
03/15/07	-76	ND[1]	5.97	ND[1]	7.28	5.24	6.18	6.39	5.65	5.57	5.65	6.38	5.33	5.96	5.88
04/03/07	-57	5.23	5.37	4.96	6.95	5.01	5.38	6.04	5.62	4.84	5.71	6.40	5.86	6.87	5.46
04/10/07	-50	5.95	5.89	5.54	7.37	5.32	5.84	6.27	5.85	5.62	5.92	6.08	5.83	5.59	5.56
04/18/07	-42	ND[1]	ND[1]	5.21	7.15	5.20	5.51	5.85	5.60	5.36	5.20	5.92	5.64	5.30	5.31
5/3/2007	-27	5.87	5.78	5.22	7.14	5.05	5.61	6.00	5.68	5.45	5.48	5.95	5.37	5.50	5.29
6/14/2007	15	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	5.86	5.47	5.95	6.04	5.56	ND[1]	ND[1]
7/2/2007	33	5.97	5.69	5.12	7.24	5.15	5.62	5.95	5.14	5.26	5.74	5.70	5.45	5.48	5.37
7/31/2007	62	6.27*	6.12*	5.31*	7.40*	5.35*	5.92*	6.25*	6.22*	6.06*	6.18*	6.56*	6.47*	5.90*	5.82*
9/5/2007	98	6.18	6.25	5.42	7.31	5.13	5.80	6.44	6.51	6.49	6.53	6.55	6.40	5.52	5.47
10/25/2007	148	6.59	6.71	5.47	7.44	5.26	5.77	6.73	6.56	6.68	6.59	6.69	6.48	5.65	5.61
1/7/2008	222	5.98	6.28	5.40	7.46	5.11	5.76	6.76	6.67	6.41	6.59	6.76	6.03	5.36	5.58
2/28/2008	274	6.18	6.42	5.53	7.45	5.28	5.89	6.80	6.85	6.15	6.43	6.79	6.37	5.68	5.63
5/7/2008	343	ND[1]	ND[1]	5.43	7.38	4.80	5.77	6.69	6.83	5.92	6.39	6.69	6.34	5.27	5.09
7/23/2008	420	ND[1]	ND[1]	NR[2]	NR[2]	NR[2]	NR[2]	NR[2]	NR[2]	NR[2]	NR[2]	NR[2]	NR[2]	NR[2]	NR[2]
12/15/2008	565	ND[1]	ND[1]	4.87	ND[1]	5.23	ND[1]	6.73	6.31	5.56	5.48	6.71	6.40	5.65	ND[1]

*pH values done in laboratory due to malfunctioning YSI meter.

[1]ND, Not Determined

[2]NR, Not Reported. Data not reported due to a field meter malfunction.

Table 5.33. Dissolved Oxygen (DO) in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	1.09	0.59	0.84	0.88	3.64	2.25	1.81	1.05	2.32	2.99	2.99	4.48
03/15/07	-76	8.56	5.12	ND[1]	0.31	1.64	1.12	4.46	2.81	1.50	1.66	3.15	3.38	3.14	5.19
04/03/07	-57	5.88	8.27	10.1	0.69	2.74	1.06	3.28	3.06	2.36	3.16	3.10	5.18	3.10	5.11
04/10/07	-50	8.00	7.61	-0.13	0.48	3.11	1.95	2.98	2.71	2.61	2.85	2.82	2.97	2.79	4.45
04/18/07	-42	ND[1]	ND[1]	0.61	0.47	3.88	2.09	2.98	2.13	2.29	0.73	3.02	3.00	3.37	4.72
5/3/2007	-27	7.16	8.04	1.35	1.42	2.00	1.75	3.14	2.53	1.70	1.71	2.48	5.91	2.61	4.27
6/14/2007	15	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	0.52	0.45	0.46	0.28	1.06	ND[1]	ND[1]
7/2/2007	33	3.16	1.67	1.04	0.42	1.56	1.65	0.40	0.18	0.28	0.15	0.16	2.09	2.41	4.23
7/31/2007	62	NR[2]	NR[2]	2.13	0.95	3.02	NR[1]	NR[2]	NR[2]	NR[2]	NR[2]	NR[2]	2.60	3.59	5.17
9/5/2007	98	0.03	0.00	0.01	0.01	2.45	0	0.22	-1.23	0.08	0.01	0.23	0.27	2.88	3.90
10/25/2007	148	NR[2]	NR[2]	NR[2]	NR[2]	2.57	0.49	NR[2]	0.44	0.36	0.35	0.41	NR[2]	3.86	4.05
1/7/2008	222	1.86	0.94	2.25	0.29	1.42	2.30	0.65	0.34	0.28	0.25	0.69	0.87	3.04	5.93
2/28/2008	274	5.08	4.40	1.44	0.04	1.96	2.74	0.34	-0.29	0.05	0.11	0.28	0.33	3.29	4.18
5/7/2008	343	ND[1]	ND[1]	1.29	0.85	6.48	4.30	0.39	0.40	0.83	0.52	0.54	0.34	4.68	6.50
7/23/2008	420	ND[1]	ND[1]	0.77	0.07	5.32	0.00	0.0	0.0	0.0	0.0	0	0	3.44	4.58
12/15/2008	565	ND[1]	ND[1]	2.13	ND[1]	1.84	ND[1]	0.21	0.19	1.02	0.69	0.22	0.27	3.45	ND[1]

[1]ND, Not Determined

[2]NR, Not Reported. Data not reported due to a YSI field meter malfunction.

Table 5.34. Temperature (^{o}C) in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	10.5	8.99	10.1	9.76	9.90	10.0	9.79	9.31	9.95	9.00	9.47	10.4
03/15/07	-76	10.3	10.3	ND[1]	10.4	9.75	9.79	10.3	10.0	9.76	8.72	9.85	8.10	9.87	9.32
04/03/07	-57	10.6	10.0	12.2	11.6	10.2	10.4	10.4	10.1	9.73	9.43	9.68	9.82	10.5	9.87
04/10/07	-50	8.90	8.34	10.8	10.3	9.90	9.99	9.57	10.3	9.60	9.02	9.03	8.74	10.0	8.82
04/18/07	-42	ND[1]	ND[1]	10.0	9.57	7.95	9.71	9.55	9.33	9.35	9.02	9.24	9.46	10.3	9.71
5/3/2007	-27	13.8	11.7	12.0	11.6	9.77	11.0	10.4	10.1	10.9	8.65	10.2	8.52	10.9	10.1
6/14/2007	15	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	10.8	10.7	9.31	10.4	10.0	ND[1]	ND[1]
7/2/2007	33	15.6	13.4	11.7	12.6	11.0	10.9	10.5	11.2	11.3	10.5	10.7	10.9	11.4	10.6
7/31/2007	62	NR[2]	NR[2]	12.2	13.4	12.8	NR[2]	NR[2]	NR[2]	NR[2]	NR[2]	12.2	13.0	12.1	11.5
9/5/2007	98	16.7	15.1	12.4	14.6	12.7	11.8	11.5	12.1	12.6	12.3	12.1	13.9	11.7	11.6
10/25/2007	148	12.2	12.2	12.3	12.8	11.9	11.7	11.2	12.2	11.7	13.0	11.7	13.4	11.4	11.4
1/7/2008	222	12.1	12.7	11.9	11.5	11.5	11.1	11.2	11.4	10.9	11.0	11.3	10.8	11.2	11.0
2/28/2008	274	7.68	9.02	10.5	8.63	9.10	9.06	10.4	9.06	9.01	8.98	10.3	7.47	10.1	9.45
5/7/2008	343	ND[1]	ND[1]	12.3	11.9	9.67	11.2	9.57	10.4	11.3	9.17	9.44	7.85	10.2	9.30
7/23/2008	420	ND[1]	ND[1]	12.2	13.5	11.4	11.3	10.95	11.4	12.6	11.15	11.16	11.7	11.7	10.56
12/15/2008	565	ND[1]	ND[1]	12.7	ND[1]	10.9	ND[1]	10.3	11.1	11.0	11.6	10.7	10.6	10.1	ND[1]

[1]ND, Not Determined

[2]NR, Not Reported. Data not reported due to a YSI field meter malfunction.

Table 5.35. Depth to water (ft below top of casing; TOC) in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	8.78	8.23	7.79	8.38	7.25	5.48	8.22	6.97	8.08	8.20	7.10	7.00
03/15/07	-76	ND[1]	ND[1]	ND[1]	8.90	8.44	9.12	7.98	6.22	9.00	7.72	8.74	8.91	7.78	7.68
04/03/07	-57	ND[1]	ND[1]	9.46	8.58	8.26	8.96	7.67	5.88	8.84	7.37	8.45	8.57	7.62	7.43
04/10/07	-50	ND[1]	ND[1]	9.60	8.70	8.46	9.14	7.92	6.18	9.01	7.67	8.74	8.83	7.78	7.64
04/18/07	-42	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]
5/3/2007	-27	ND[1]	ND[1]	9.18	8.55	7.94	8.67	7.44	5.70	8.53	7.15	8.25	8.31	7.30	ND[1]
6/14/2007	15	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	6.88	9.67	8.41	9.44	9.56	ND[1]	ND[1]
7/2/2007	33	ND[1]	ND[1]	ND[1]	9.37	9.17	9.85	9.68	6.94	9.73	5.47	9.47	9.61	8.50	8.41
7/31/2007	62	ND[1]	ND[1]	9.65	8.83	8.59	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	8.87	9.01	7.90	7.84
9/5/2007	98	ND[1]	ND[1]	10.05	9.15	8.87	9.56	8.30	6.54	9.40	8.05	9.16	9.22	8.25	8.02
10/25/2007	148	ND[1]	ND[1]	9.86	9.02	8.91	9.55	8.44	ND[1]	9.44	8.23	9.22	9.37	8.21	8.20
1/7/2008	222	ND[1]	ND[1]	8.10	7.32	7.03	7.67	6.70	4.90	7.53	6.18	7.32	7.55	6.41	6.22
2/28/2008	274	ND[1]	ND[1]	8.15	7.29	7.05	7.78	6.60	4.85	7.62	6.27	7.45	7.60	6.50	6.30
5/7/2008	343	ND[1]	ND[1]	8.53	7.67	7.36	8.13	6.97	4.33	7.89	7.74	7.79	8.10	7.79	7.68
7/23/2008	420	ND[1]	ND[1]	8.90	8.04	8.05	8.65	7.50	5.72	8.54	7.32	8.31	8.46	7.31	7.26
12/15/2008	565	ND[1]	ND[1]	7.80	ND[1]	6.35	ND[1]	5.90	4.20	7.05	5.53	6.78	7.88	5.87	ND[1]

5.6.4 Anions

5.6.4.1 Bromide

A tracer test was performed to evaluate/verify local hydrogeological characteristics and to accurately determine the extent of the capture zone and radius of influence of each extraction well in the treatment system. The tracer test consisted of amending 4,100 L of site groundwater with 12.5 kg of sodium bromide as a conservative tracer. Bromide amended groundwater was metered into the recirculated groundwater at a rate of approximately 57 LPH over a period of three days. The experimental details are provided in Section 5.4.2 and bromide data are provided in **Figure 5.45** and **Table 5.36.** Bromide was detected at each of the TZMWs within 7 days of the addition period (the first sampling event). The concentrations in each well were similar, ranging from 13.3 mg/L in 157MW-6D to 20.5 mg/L in 157MW-4. Similar concentrations were detected in the two EWs. The data clearly showed that all of the TZMWs were hydraulically connected to the EWs. No bromide was detected in any of the upgradient or downgradient CZMWs with the exception of one point at 148 days in 157MW-8D (1.43. mg/L). Bromide was not detected at any of the later sampling points in this well so we assume that this well was not significantly impacted by the treatment system.

5.6.4.2 Naturally Occurring Anions

Several naturally occurring anions were measured to evaluate the geochemistry of the aquifer, and to determine changes caused by the addition of cheese whey. Among the anions measured, nitrate (NO_3^-) was only detected in wells 157MW-1 and 157MW-2 **(Table 5.37)**, and concentrations in these wells were generally < 0.5 mg/L, and nitrite (NO_2^-) was not detected in any of the wells **(Table 5.38)**. Similarly, with a few exceptions, orthophosphate **(Table 5.39)** was below detection in the aquifer. Sulfate concentrations ranged from approximately 7 to 27 mg/L during the several rounds of baseline sampling, and they were reasonably constant in each well as a function of time prior to cheese whey addition (**Figure 5.46** and **Table 5.40).** After the aquifer was amended with cheese whey, the sulfate concentrations declined in all of the TZMWs beginning approximately 3 months after injection. This reduction in sulfate is expected, and consistent with the occurrence of biological sulfate reduction (sulfide was not measured). The sulfate concentration rebounded in wells 157MW-5, 157MW-6S and 157MW-6D during the latter half of the demonstration period, but remained low in the other TZMWs. Chloride concentrations ranged from approximately 2 mg/L to 30 mg/L in baseline sampling, and as with sulfate, values were consistent with time in each well during the baseline events **(Table 5.41)**. Chloride was observed to increase moderately in the TMZWs, presumably due to the addition of cheese whey. Concentrations remained below 65 mg/L in all TMZWs throughout the demonstration period.

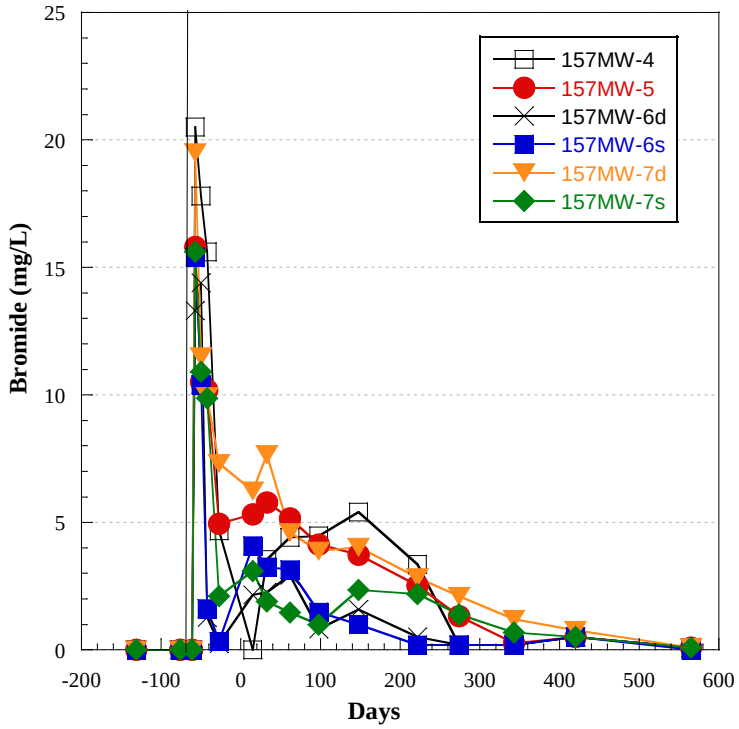


Figure 5.45. Bromide in TZMWs during the course of the demonstration. Bromide was added from Days -66 to -64.

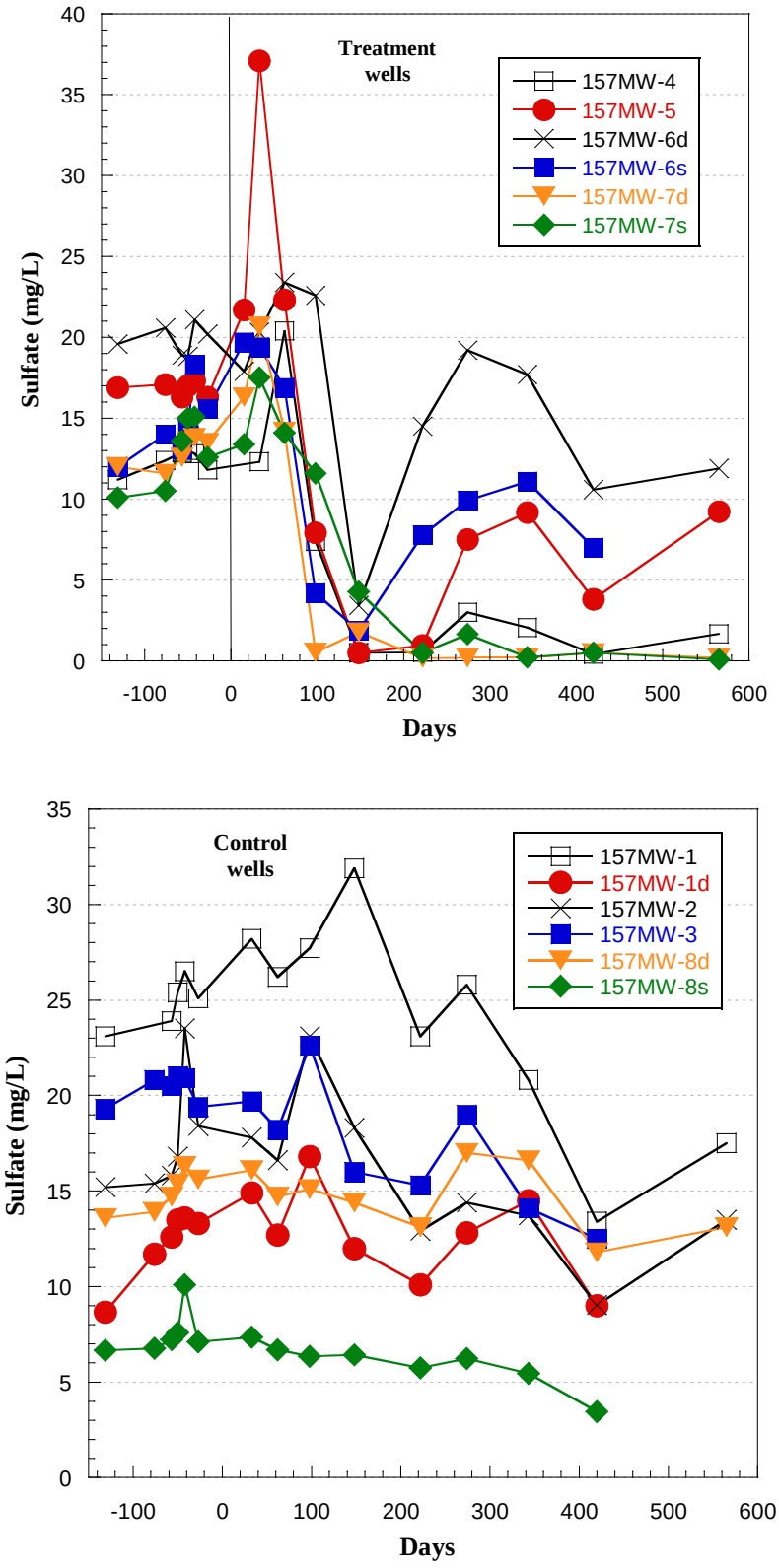


Figure 5.46. Sulfate concentration (mg/L) in treatment wells (top panel) and control wells (bottom panel) during the course of the demonstration.

Table 5.36. Bromide (mg/L) in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]
03/15/07	-76	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]
03/30/07	-61	**14.0**	**13.5**	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]
04/03/07	-57	**11.8**	**16.3**	<1	<0.1	<0.1	<0.1	**20.5**	**15.8**	**13.3**	**15.4**	**19.5**	**15.6**	<0.1	<0.1
04/10/07	-50	**6.81**	**11.3**	<0.1	<0.1	<0.1	<0.1	**17.8**	**10.5**	**14.4**	**10.4**	**11.5**	**10.9**	<0.1	<0.1
04/18/07	-42	ND[1]	ND[1]	<0.2	<0.2	<0.2	0.36	**15.6**	**10.2**	**1.27**	**1.61**	**9.94**	**9.87**	<0.2	<0.2
5/3/2007	-27	**0.45**	**6.76**	**0.26**	<0.2	<0.2	<0.2	**4.68**	**4.95**	**0.25**	**0.34**	**7.31**	**2.10**	<0.2	<0.2
6/14/2007	15	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	**5.31**	**2.16**	**4.09**	**6.23**	**3.09**	ND[1]	ND[1]
7/2/2007	33	**1.39**	**8.14**	<0.5	<0.5	<0.5	<0.5	**3.55**	**5.78**	**2.26**	**3.25**	**7.67**	**1.89**	<0.5	<0.5
7/31/2007	62	**1.16**	**6.79**	<0.5	<0.5	<0.5	<0.5	**4.41**	**5.17**	**2.92**	**3.14**	**4.60**	**1.47**	<0.5	0.5
9/5/2007	98	**0.2**	**4.42**	<0.5	<0.5	<0.5	<0.5	**4.46**	**4.13**	**0.82**	**1.48**	**3.88**	**1.00**	<0.5	<0.5
10/25/2007	148	**2.05**	**3.89**	<0.5	<0.5	<0.5	<0.5	**5.41**	**3.73**	**1.58**	**1.00**	**4.03**	**2.35**	**1.43**	<0.5
1/7/2008	222	**0.27**	**2.62**	<0.5	<0.5	<0.5	<0.5	**3.35**	**2.53**	<0.5	**0.19**	**2.83**	**2.19**	<0.5	<0.5
2/28/2008	274	<0.2	**4.44**	<0.2	<0.2	<0.2	<0.2	<0.2	**1.32**	<0.2	<0.2	**2.10**	**1.40**	<0.2	<0.2
5/7/2008	343	<0.2	**4.2**	<0.2	<0.2	<0.2	<0.2	<0.2	**0.27**	<0.2	<0.2	**1.20**	**0.67**	<0.2	<0.2
7/23/2008	420	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	**0.77**	<0.5	<0.5	<0.5
12/15/2008	565	ND[1]	ND[1]	<0.1	ND[1]	<0.1	ND[1]	<0.1	<0.1	<0.1	ND[1]	<0.1	<0.1	<0.1	ND[1]

[1]ND, Not Determined

Table 5.37. Nitrate (mg/L as Nitrate-N) in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
03/15/07	-76	<2	<2	ND[1]	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
03/30/07	-61	<1	<1	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]
04/03/07	-57	<0.1	<0.1	**0.34**	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
04/10/07	-50	<0.1	<0.1	**0.31**	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
04/18/07	-42	ND[1]	ND[1]	**0.27**	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
5/3/2007	-27	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
6/14/2007	15	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	<0.1	<0.1	<0.1	<0.1	<0.1	ND[1]	ND[1]
7/2/2007	33	<0.5	<0.5	<0.5	<0.5	**0.50**	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
7/31/2007	62	<0.5	<0.5	**0.34**	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
9/5/2007	98	<0.5	<0.5	**0.38**	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
10/25/2007	148	<0.5	<0.5	**0.62**	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1/7/2008	222	<0.5	<0.5	**0.36**	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2/28/2008	274	<0.2	<0.2	**0.55**	<0.2	**0.49**	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
5/7/2008	343	<0.2	**0.14**	**0.65**	<0.2	**0.23**	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
7/23/2008	420	<0.5	<0.5	**0.32**	<0.5	**0.20**	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
12/15/2008	565	ND[1]	ND[1]	**0.32**	ND[1]	**0.43**	ND[1]	<0.1	<0.1	<0.1	ND[1]	<0.1	<0.1	<0.1	ND[1]

[1]ND, Not Determined

Table 5.38. Nitrite (mg/L as Nitrite-N) in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
03/15/07	-76	<2	<2	ND[1]	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
03/30/07	-61	<1	<1	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]
04/03/07	-57	<0.1	<0.1	<1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
04/10/07	-50	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
04/18/07	-42	ND[1]	ND[1]	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
5/3/2007	-27	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
6/14/2007	15	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	<0.1	<0.1	<0.1	<0.1	<0.1	ND	ND
7/2/2007	33	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
7/31/2007	62	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
9/5/2007	98	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
10/25/2007	148	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1/7/2008	222	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2/28/2008	274	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
5/7/2008	343	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
7/23/2008	420	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
12/15/2008	565	ND[1]	ND[1]	<0.1	ND[1]	<0.1	ND[1]	<0.1	<0.1	<0.1	ND[1]	<0.1	<0.1	<0.1	ND[1]

[1]ND, Not Determined

Table 5.39. Orthophosphate (mg/L) in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	<0.5	**0.47**	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.53	<0.5	<0.5
03/15/07	-76	<2	<2	ND[1]	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
03/30/07	-61	<1	<1	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]
04/03/07	-57	<0.1	<0.1	<1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
04/10/07	-50	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
04/18/07	-42	ND[1]	ND[1]	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
5/3/2007	-27	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
6/14/2007	15	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	<0.1	<0.1	<0.1	<0.1	<0.1	ND[1]	ND[1]
7/2/2007	33	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
7/31/2007	62	<0.5	<0.5	**0.87**	<0.5	**0.65**	<0.5	**0.63**	**0.75**	<0.5	**0.43**	<0.5	<0.5	<0.5	**0.82**
9/5/2007	98	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
10/25/2007	148	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	**1.22**
1/7/2008	222	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	**1.22**
2/28/2008	274	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
5/7/2008	343	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
7/23/2008	420	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
12/15/2008	565	ND[1]	ND[1]	<0.1	ND[1]	<0.1	ND[1]	<0.1	<0.1	<0.1	ND[1]	<0.1	<0.1	<0.1	ND[1]

[1]ND, Not Determined

Table 5.40. Sulfate (mg/L) in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	23.1	8.67	15.2	19.3	11.2	16.9	19.6	12.0	12.0	10.1	13.6	6.67
03/15/07	-76	19.1	13.4	ND[1]	11.7	15.4	20.8	12.4	17.1	20.6	14.0	11.6	10.5	13.9	6.76
03/30/07	-61	13.1	13.1	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]
04/03/07	-57	12.9	13.2	23.9	12.6	15.8	20.5	12.9	16.3	18.9	13.1	12.6	13.6	14.7	7.23
04/10/07	-50	14.4	14.5	25.4	13.5	16.8	21.0	13.0	17.0	18.8	14.3	13.6	15.0	15.4	7.60
04/18/07	-42	ND[1]	ND[1]	26.5	13.6	23.5	20.9	12.8	17.3	21.1	18.3	13.8	15.1	16.3	10.1
5/3/2007	-27	13.9	11.9	25.1	13.3	18.4	19.4	11.8	16.3	20.2	15.6	13.5	12.6	15.6	7.09
6/14/2007	15	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	21.7	17.9	19.7	16.3	13.4	ND[1]	ND[1]
7/2/2007	33	11.9	15.6	28.2	14.9	17.8	19.7	12.3	37.1	20.3	19.4	20.7	17.5	16.1	7.34
7/31/2007	62	7.05	13.8	26.2	12.7	16.6	18.2	20.4	22.3	23.4	16.9	14.2	14.1	14.7	6.69
9/5/2007	98	10.0	14.1	27.7	16.8	23.1	22.6	7.40	7.93	22.6	4.20	0.52	11.6	15.1	6.34
10/25/2007	148	2.69	2.69	31.9	12.0	18.3	16.0	<0.5	<0.5	3.41	1.87	1.79	4.28	14.4	6.42
1/7/2008	222	13.8	4.15	23.1	10.1	12.9	15.3	0.52	0.94	14.5	7.78	0.17	<0.5	13.1	5.74
2/28/2008	274	21.5	3.47	25.8	12.8	14.4	19.0	3.02	7.51	19.2	9.93	<0.2	1.65	17.0	6.23
5/7/2008	343	21.0	9.40	20.8	14.5	13.7	14.1	2.06	9.18	17.7	11.1	<0.2	0.24	16.6	5.44
7/23/2008	420	ND[1]	ND[1]	13.4	9.00	9.01	12.5	0.41	3.81	10.6	6.99	<0.5	<0.5	11.8	3.45
12/15/2008	565	ND[1]	ND[1]	17.5	ND[1]	13.5	ND[1]	1.68	9.23	11.9	ND[1]	0.21	<0.1	13.1	ND[1]

[1]ND, Not Determined

Table 5.41. Chloride (mg/L) in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	23.7	27.8	14.5	15.6	2.78	17.7	15.0	32.5	8.61	1.91	12.5	2.00
03/15/07	-76	3.92	6.83	ND[1]	27.6	15.8	13.5	3.14	17.3	13.3	23.1	8.62	1.56	13.4	1.81
03/30/07	-61	6.71	7.93	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]
04/03/07	-57	7.32	8.48	20.8	27.8	14.1	12.2	6.63	10.9	13.3	7.72	7.95	7.68	13.3	1.87
04/10/07	-50	6.32	9.44	20.0	27.8	13.2	14.2	7.55	11.2	10.9	8.59	8.47	8.48	12.8	1.85
04/18/07	-42	ND[1]	ND[1]	18.9	27.2	17.1	14.0	7.14	13	12.7	14.0	8.28	8.33	11.8	2.05
5/3/2007	-27	20.7	45.3	19.4	27.6	12.5	12.3	3.64	19.8	12.9	14.8	7.56	28.7	11.4	1.50
6/14/2007	15	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	42.5*	27.1*	49.7*	41.9*	33.5*	ND[1]	ND[1]
7/2/2007	33	44.7	31.3	41.4	26.5	14.5	14.4	20.1	47.8	22.7	48.3	43.6	26.3	13.3	1.54
7/31/2007	62	51.7	31.1	28.6	27.1	15.6	12.1	41.7	42.8	36.1	49.6	47.5	31.5	12.6	1.39
9/5/2007	98	52.4	37.8	17.5	26.5	20.3	11.8	42.9	39.8	18.6	36.8	46.4	21.8	10.2	1.33
10/25/2007	148	53.5	24.0	21.7	26.0	20.7	31.5	45.4	57.3	29.3	57.7	53.4	40.7	11.3	2.05
1/7/2008	222	41.8	60.7	20.7	25.7	19.0	11.4	57.8	46.9	11.3	30.4	51.5	44.2	8.20	1.36
2/28/2008	274	43.3	79.0	25.8	29.2	36.2	14.7	45.1	34.1	12.7	44.7	53.3	49.3	7.76	4.70
5/7/2008	343	40.6	69.0	31.7	29.7	69.6	27.5	47.8	42.2	17.5	61.9	59.4	27.1	8.40	4.08
7/23/2008	420	ND[1]	ND[1]	24.7	24.8	63.2	26.7	49.4	30.2	16.6	46.2	61.6	20.7	7.39	5.47
12/15/2008	565	ND[1]	ND[1]	24.2	ND[1]	35.3	ND[1]	52.1	44.9	19.7	ND[1]	18.2	51.2	7.77	ND[1]

[1]ND, Not Determined

*Value exceeds highest calibration standard by >15%

5.6.5 Metals

Dissolved iron (Fe) and manganese (Mn) were measured periodically throughout the demonstration to assess the extent of mobilization of these metals during groundwater treatment. Other metals and cations were not measured.

5.6.5.1 Dissolved Iron

The concentration of dissolved iron in the demonstration monitoring wells was generally < 0.1 mg/L during background sampling **(Figure 5.47 and Table 5.42)**. There was no significant increase in any of the CZMWs. In the TZMWs, however, dissolved Fe increased significantly, reaching between 7 and 170 mg/L in the various wells. This is consistent with biological iron reduction during cell growth on cheese whey carbon. The smallest increases were observed in upgradient TZMWs 157MW-6S and 157MW-6D, which is consistent with both the lower sustained TOC concentrations in these wells and the higher overall ORP values after the initial 3 months of treatment.

5.6.5.2 Dissolved Manganese

With the exception of the deep bedrock well, which had natural Mn concentrations of 0.3 mg/L during background sampling, all other wells had concentrations < 0.1 mg/L **(Figure 5.47 and Table 5.43)**. There was no significant increase in any of the CZMWs. However, as with Fe, dissolved Mn increased significantly in all of the TZMWs after whey addition, reaching between 8 and 90 mg/L in the various wells. These increases are consistent with biological manganese reduction. AS with Fe, the smallest concentration increases were observed in wells 157MW-6S and 157MW-6D.

5.6.6 Methane

Concentrations of dissolved methane were measured at four points during the course of the demonstration to evaluate increases in this gas due to methanogenesis occurring under anoxic conditions in the aquifer **(Table 5.44)**. Methane was detected naturally in well 157MW-1D at > 1 mg/L, but was < 10 μg/L in all of the other CZMWs wells during the various sampling events, all of which occurred after the addition of cheese whey. Methane was detected at > 5 mg/L and at concentrations as high as 20 mg/L in TZMWs 157MW-6S, 157MW-7S, and 157MW-7D. Concentrations in the other TZMWs were increased compared to background, but remained below 1 mg/L during the events.

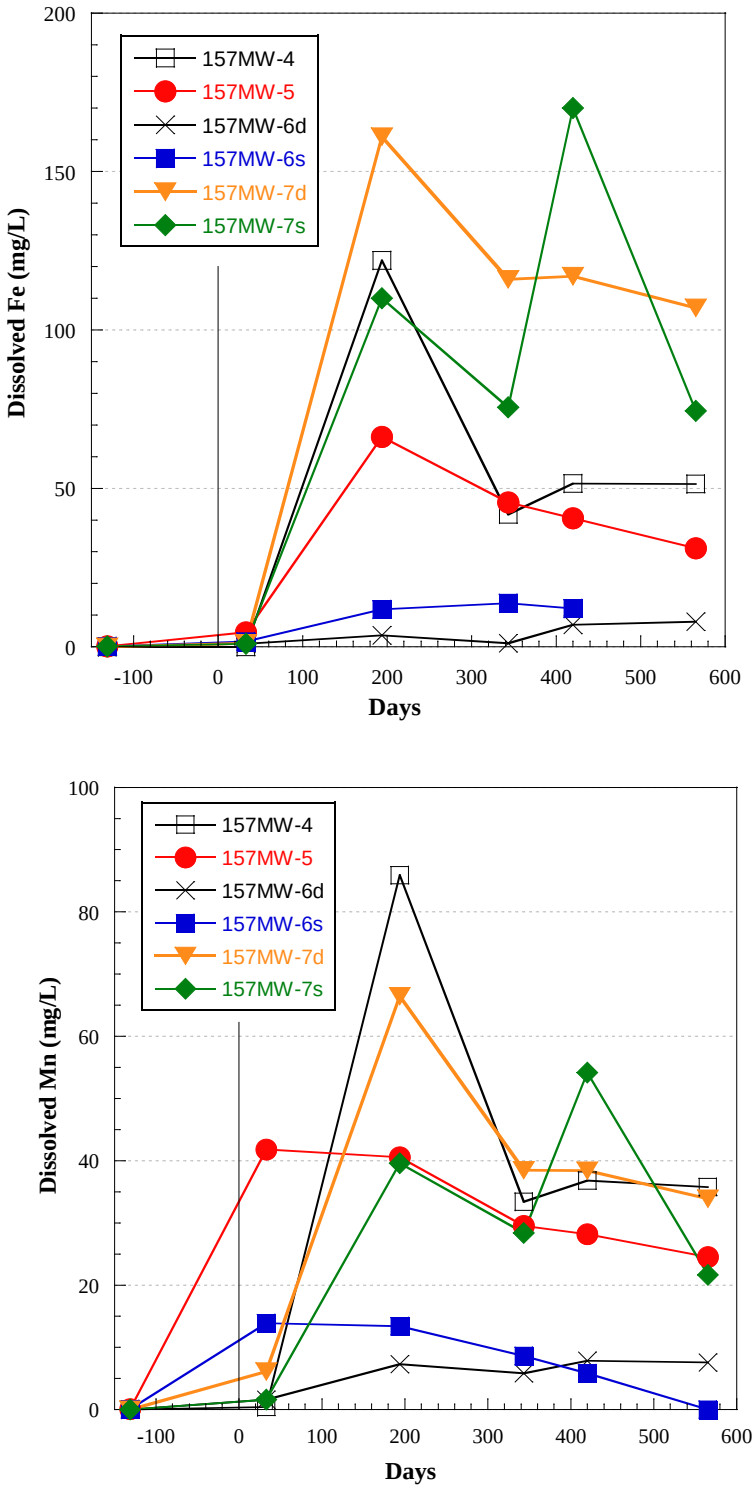


Figure 5.47. Dissolved iron (top panel) and manganese (bottom panel) concentration (mg/L) in treatment wells during the course of the demonstration.

Table 5.42. Dissolved Iron (mg/L) in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	0.034	0.97	0.025	0.032	0.024	0.12	0.057	0.14	0.022	0.12	0.034	0.023
7/2/2007	33	< 0.05	5.92	< 0.05	1.24	< 0.05	< 0.05	< 0.05	4.63	0.92	1.68	1.18	0.91	< 0.05	0.32
2/28/2008	194	6.25	120	< 0.10	0.51	< 0.10	< 0.10	122	66.3	3.63	11.9	161	110	< 0.10	< 0.10
5/7/2008	343	4.02	58.6	<100	0.55	< 0.10	< 0.10	41.9	45.6	1.08	13.7	116	75.6	< 0.10	< 0.10
7/23/2008	420	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	51.5	40.6	6.95	12.1	117	170	ND[1]	ND[1]
12/15/2008	565	ND[1]	ND[1]	0.097	ND[1]	0.056	ND[1]	51.4	31.2	7.86	ND[1]	107	74.5	0.41	ND[1]

[1]ND, Not Determined

Table 5.43. Dissolved Manganese (mg/L) Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells.

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
1/17/2007	-131	ND[1]	ND[1]	0.02	0.37	0.046	0.039	0.008	0.072	0.023	0.09	0.015	0.027	0.086	0.013
7/2/2007	33	0.09	5.27	0.024	0.17	0.015	<0.008	0.426	41.8	1.6	13.9	6.1	1.58	0.004	38.2
2/28/2008	194	6.38	70	0.027	0.17	0.061	0.025	85.9	40.6	7.28	13.4	66.5	39.6	0.1	<0.015
5/7/2008	343	4.58	34.6	0.028	0.14	0.059	0.106	33.4	29.5	5.87	8.64	38.5	28.4	0.104	<0.015
7/23/2008	420	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	36.8	28.2	7.86	5.86	38.4	54.2	ND[1]	ND[1]
12/15/2008	565	ND[1]	ND[1]	0.026	ND[1]	0.039	ND[1]	35.8	24.5	7.6	ND[1]	33.9	21.7	0.19	ND[1]

[1]ND, Not Determined

Table 5.44. Dissolved Methane (μg/L) in Extraction and Monitoring Wells during the Demonstration. Columns shaded in blue contain data from treatment wells, columns in tan are from the groundwater extraction wells, and unshaded columns are from control wells

Date	Days	157EW-1	157EW-2	157MW-1	157MW-1D	157MW-2	157MW-3	157MW-4	157MW-5	157MW-6D	157MW-6S	157MW-7D	157MW-7S	157MW-8D	157MW-8S
10/25/2007	148	**95.0**	**11.8**	<5	**1180**	<5	<5	**4.44**	**639**	<5	<5	**15.6**	**6.24**	<5	**10.5**
2/28/2008	194	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	**1.33**	**213**	**641**	**2.84**	**129**	**14400**	**13800**	ND[1]	ND[1]
5/7/2008	343	**257**	**270**	ND[1]	ND[1]	<2	ND[1]	**5.78**	**41.1**	<2	**4.39**	**14700**	**34000**	ND[1]	ND[1]
7/23/2008	420	ND[1]	ND[1]	**1.36**	**1230**	**1.54**	**1.47**	**390**	**80.9**	**1.02**	**6100**	**20100**	**18400**	**1.72**	**1.54**

[1]ND, Not Determined

6.0 Performance Assessment

6.1 Performance Criteria

Performance objectives were established for this demonstration to provide a basis for evaluating the results of the *in situ* remediation approach for explosives in groundwater. Performance criteria were selected based on factors that would likely be considered when bringing the proposed technology to full-scale application. The performance objectives are provided in Table 3.1, and discussed in Sections 3.1 to 3.4 in this document.

As summarized in Section 3.0 and subsections therein, the critical performance objectives for this demonstration were achieved. The following subsections summarize the data collected and provide an assessment of the performance objectives, including the extent to which the criteria were achieved.

6.2 Treatment of Explosives in Groundwater

6.2.1 TNT, RDX, and HMX

The key performance objective of this demonstration was to reduce the explosives RDX, HMX, and TNT in groundwater at Picatinny to concentrations that are below levels of regulatory concern. As previously noted, those values are 2 μg/L for TNT and RDX, and 400 μg/L for HMX (MCGL values; US EPA, 2004). In addition, New Jersey has established Interim Ground Water Quality Criteria for both TNT (1 μg/L) and RDX (0.3 μg/L) that are somewhat lower than the Federal MCGL. The key performance objective for this demonstration was achieved. Concentrations of TNT in the TZMWs declined rapidly after the initial cheese whey addition. TNT concentrations were below analytical detection limits (PQL = 0.25 μg/L) in all of the TZMWs by Day 62 of the study, and remained at or below this concentration in all TZMWs except 157MW-6S throughout the remainder of the demonstration (see Section 5.6.2 for details). RDX biodegradation occurred somewhat more slowly than for TNT, but RDX concentrations declined from a plot average of 66 μg/L just prior to cheese whey addition, to < 1.5 μg/L in 5/6 TZMWs after 148 days of treatment. Moreover, on Day 565, more than 1 year after the final cheese whey injection, the concentration of RDX in all of the downgradient TZMWs was < 0.2 μg/L. A significant decline in HMX also was observed in all wells, and by Day 274 each of the 4 downgradient TZMWs had HMX concentrations < 0.4 μg/L. A slight rebound was observed in Well 157MW-5 at Day 565 (384 days after the last cheese whey injection) but HMX remained < 1 μg/L in each of the other wells throughout the remainder of the study. Several other nitroaromatics, including 1,3,5-TNB, 2,4-DNT, and 2,6-DNT were also effectively treated by the cheese whey injection. The data from the downgradient TZMWs clearly showed that the addition of cheese whey to the Picatinny aquifer effectively promoted biodegradation of TNT, RDX, and HMX to sub μg/L concentrations. Moreover, as long as TOC concentrations were

maintained > 5 mg/L, rebound of these explosives was not observed. Thus, the potential for long-term effectiveness of this semi-passive groundwater ER approach appears to be very good.

6.2.2 Interference with USEPA 8330 Analysis of RDX and HMX

One critical issue that occurred during this demonstration was the apparent interference of degradation intermediates of cheese whey with analysis of RDX and HMX by USEPA Method 8330. This method relies upon high performance liquid chromatography (HPLC) to separate explosives and a UV [photodiode array (PDA)] detector to measure quantities of each via peak area. However, because the analytes are not quantified via mass spectrometer, the method can be prone to analytical interference. During this study, beginning on Day 148 days, the contract analytical laboratory performing USEPA 8330 analysis for explosives reported analytical interference with RDX in the TZMWs with the highest TOC concentrations. Because such interference was not observed prior to this point, it is likely that the one or more degradation products (rather than the parent compounds) from the cheese whey eluted near RDX and HMX in the 8330 analysis and were falsely identified as these compounds RDX (i.e., false positive). Our analytical laboratory (Shaw) has observed similar interference issues in samples receiving high concentrations of emulsified vegetable oil, several weeks after oil addition, suggesting a similar interference via a degradation intermediate (Dr. Randi Rothmel, Shaw Laboratory director, pers comm.) The results of a PDA scan on the samples in question for RDX further confirmed that the peak present via 8330 was not RDX as the shape of the peak in the sample and that of the RDX standard were different. Values from a confirmation column with a different packing material (phenyl hexyl column) were also appreciably higher than expected for several TZMWs based on initial concentrations in the aquifer and degradation trends to that point. No interference was reported for any of the wells outside of the treatment area.

Because of the analytical issues observed with samples from several of the TZMWs on Day 148 and for several events thereafter using EPA 8330 analysis, all extracts (after solid phase extraction) from samples exhibiting interference were reanalyzed with a second method utilizing liquid-chromatography/mass-spectrometry (LC/MS) in the laboratory of Dr. Jalal Hawari at the NRC Biotechnology Research Institute in Montreal, Canada. The MDL values for RDX and HMX using this method were 0.01 mg/L and 0.02 mg/L, respectively, in the sample extracts. However, because the explosives were concentrated 50x via SPE prior to analysis, the MDL values were reduced accordingly to ~ 0.2 μg/L and 0.4 μg/L, respectively. The LC/MS analysis provided comparable results to EPA 8330 in wells where both methods were used, and in which interference with method EPA 8330 was not observed as shown for 157MW-3, 157MW-6D, and 157MW-6S in **Table 6.1**. These data suggest that it is important to closely examine explosives data generated via EPA Method 8330 in instances in which high concentrations of TOC have been added to an aquifer to promote anaerobic biodegradation of these compounds. The method appears to be prone to analytical interference and false positives under such conditions.

Table 6.1. Comparison of RDX and HMX Concentrations by LC/MS and EPA 8330.

Sample	Day	LC/MS (mg/L)[1]		EPA 8330 (mg/L)	
		RDX	HMX	RDX	HMX
157MW-3	148	0.39	0.51	0.32	0.55
157MW-3	222	0.51	0.62	0.55	0.72
157MW-6D	222	0.15	0.062	0.16	0.076
157MW-6S	420	0.24	NA[2]	0.25	NA
157MW-6D	420	0.33	NA	0.34	NA

[1] Values are from SPE extracts and are not corrected for dilution.

[2] NA: Not analyzed.

6.3 Accumulation of Degradation Intermediates

Another critical performance objective for this demonstration was to show that there was no long-term accumulation of common daughter products of TNT and RDX biodegradation, incllluding MNX, DNT and TNX (for RDX) and 2-ADNT, 4-ADNT, 2,4-DANT, or 2,6-DANT (for TNT). This performance objective was met during the study. Two of the most common TNT daughter products, 4-ADNT and 2-ADNT were present from ~ 1 to 120 μg/L in groundwater monitoring wells at the demonstration site during baseline sampling, either because they were released from the facility during processing, or because they formed after disposal to land surface via natural biological reactions. A rapid reduction in the concentrations of both of these compounds in groundwater was observed following injection of cheese whey. Neither was detected above 0.25 μg/L in the TZMWs by Day 148. For each of the downgradient TZMWs concentrations of these compounds remained below 0.25 μg/L through Day 420 (the final day of sampling for these intermediates). 2,4-DANT and 2,6-DANT, each of which is an expected degradation intermediate of TNT during anaerobic treatment, increased in the TZMWs as TNT degraded and then declined in concentration to below their respective PQL values by Day 98 and for the duration of the demonstration in all downgradient TZMWs 157MW-4, 157MW-5 157MW-7S and 157MW-7D**.** Thus, no accumulation of typical TNT degradation intermediates was indicated.

The concentrations of the common RDX daughter products MNX, DNX, and TNX increased in the TZMWs during the demonstration. However, the total concentrations were < 20 μg/L in all cases, and generally much lower, and all three nitroso-derivatives were transient. A significant decrease in the concentrations of each of these daughter products was observed during the demonstration, and all were near or below detection by Day 420 of groundwater monitoring. All

three products remained below detection in TZMWs sampled on Day 565. In addition, on Day 199, each of the TZMWs except 157MW-6S was analyzed for NDAB and MEDINA. Three of the CZMWs were also analyzed for comparison. Neither of these intermediates (which form after ring cleavage of RDX) were detected in the test or control wells at concentrations exceeding the MDL of 10 μg/L. Overall, the data indicate that known intermediates of RDX degradation by anaerobic processes, including the three nitroso-derivatives, MEDINA and NDAB are unlikely to accumulate during in situ anaerobic bioremediation explosives using cheese whey as a cosubstrate.

6.4 Adequate Distribution of Cosubstrate

A significant increase in TOC concentration within the treatment zone was observed following the initial system operation and injection of cheese whey. TOC in all wells in all TZMWs quickly reached concentrations exceeding 90 mg/L after the initial injection, with some wells exceeding 200 mg/L. The initial goal was to achieve at least 10 mg/L TOC in each well. TOC in monitoring wells outside of the treatment zone did not increase above the background concentration. Significant increases in TOC were again observed after the third and fourth injection events in all wells except 157MW-6S and 157MW-6D. These wells were upgradient of the injection well, and it is presumed that they were not impacted by the later whey additions due to an increased rate (or slight shift in direction) of groundwater flow in the area. The gradient in the treatment area was relatively flat and prone to alterations with the water table.

During the initial model simulations, the system was operated in a "3 days on/15 days off" cycle, with cheese whey injection occurring during the on cycles. Based on this mode of operation, and assuming consistent hydrogeologic conditions (groundwater flow rate and direction), the zone of influence after 180 days of operation was reach Wells 157MW-3 (upgradient) and 157MW8S/D (downgradient) as shown in **Figure 6.1**. In reality, the zone of influence did not extend this far upgradient or downgradient (the estimated extent of influence is shown as the white line in **Figure 6.1**). The smaller than expected zone of influence most likely had two contributing factors as follows:

(1) The operational cycle of the system was modified from and initial "3 days on/15 days off" cycle to "3 days on/ 40-80 days off" during the first 180 days of operation. This change was made based on the initial observation that the cheese whey was widely distributed at high concentrations during the injection cycle and that concentrations sufficient to promote explosives biodegradation persisted far beyond the expected 15 days. The zone of influence of the system was probably smaller due the extension in the system "off" cycle. However, for practical operation fewer pumping cycles result in less expense due to O&M and injection well fouling, so this trade-off was made during system operation.

(2) The groundwater flow rate and or direction may have shifted somewhat during system operation due to high rainfall (and an increase of nearly 2 ft in groundwater elevation as described in Section 5.6. It is presumed that this shift resulted in a reduced impact of cheese whey injections on upgradient well pair 157MW-6S/6D after the initial injections on Day 0 and Day 41, respectively. TOC increased significantly in this well pair after the initial injection at Day 0 and somewhat after Day 41, but there was no significant increase after the subsequent injection. The downgradient TZMWs were impacted by the later injections. Thus, it appears that the system influence on the upgradient wells during pumping was much reduced during the latter injection cycles. The fact that this well pair was not influenced during later events provided an opportunity to evaluate contaminant rebound as TOC declined in the plot. For the most part, the downgradient TZMWs maintained a high enough TOC concentration during the demonstration that rebound was not observed.

Overall, the intermittent pumping design was extremely effective at distributing cosubstrate within the core treatment zone as indicated by TOC concentrations in downgradient wells. It is anticipated that a wider zone of influence could have been achieved with more frequent pumping cycles. However, the trade-off for increased operation is an increased likelihood of injection well fouling (which did not occur during this demonstration) as well as increased O&M costs, as daily visits to the system (and multiple filter changes) were required during the active treatment phases. For full-scale operation, lower O&M costs for *in situ* system are always desirable.

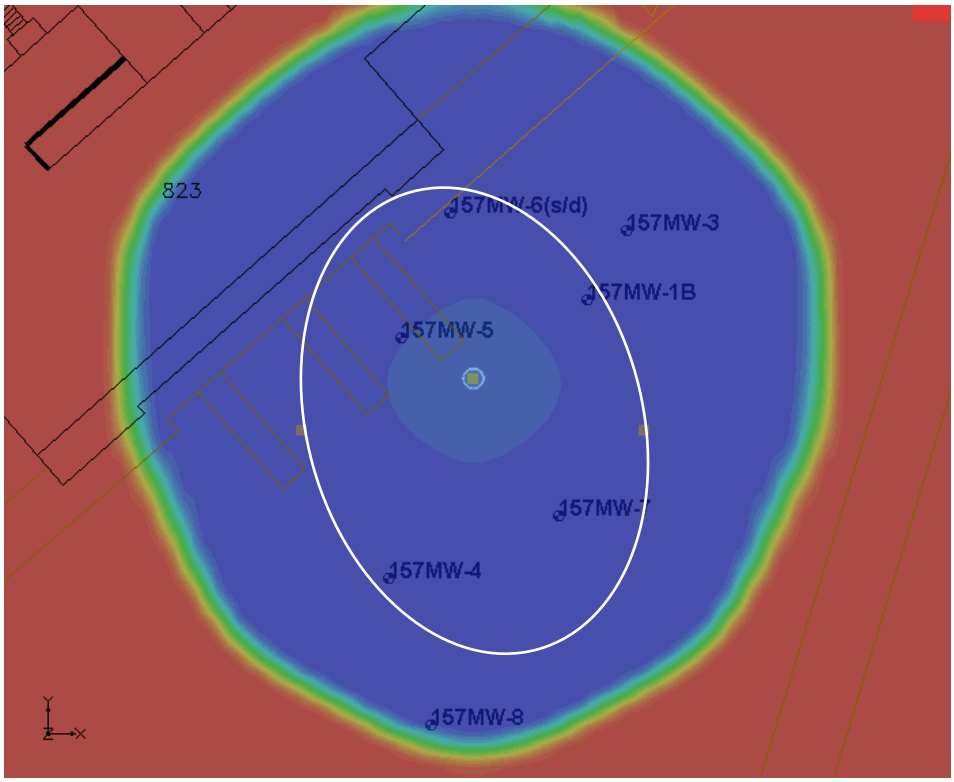


Figure 6.1. Simulated treatment zone (blue shaded area) after 180 days of system operation compared to estimated actual treatment zone (white outline). During the simulation the EWs (square symbols) were operated at 5 GPM on a 3 day on/15 days off schedule. During the demonstration, the system was operated at ~ 3 days on/40-80 days off during the first 180 days of operation.

6.5 Biofouling Control in Injection Well

Microbial biofouling is a significant concern with any *in situ* remedial system, and particularly with those requiring active pumping. During this demonstration, techniques to control biofouling included: (1) pumping groundwater intermittently rather than continuously, and reducing the active pumping phase as much as possible, and (2) injecting large quantities of cosubstrate during the pumping phase; and (3) injecting groundwater through a pressurized packer to promote movement of water into the formation. The combination of these techniques proved effective to control biofouling during a previous demonstration of in situ perchlorate treatment at the Whittaker-Bermite site in California (Hatzinger and Lippincott, 2009). In

addition, the injection well was designed with a downhole pump connected to a recirculation loop so that the anti-fouling amendment Tetrakis(hydroxymethyl)phosphonium sulfate (THPS) could be added and distributed within the well if necessary based on pressure in the injection well. During the demonstration, addition of THPS was not necessary because the first three strategies were effective at controlling well fouling. Significant pressure increases were not observed in the IW during the four pumping phases, so additional control or well rehabilitation measures were not necessary. Most importantly, using the pumping design primarily as a means to mix cosubstrate into the aquifer was determined to significantly reduce the potential for biofouling and the associated costs with this issue.

7.0 Cost Assessment

This section provides detailed cost information and an economic analysis for *in situ* bioremediation of energetic compounds in groundwater.

7.1 Cost Model

In order to evaluate the cost of a potential full-scale bioremediation program, and compare it against other remedial approaches, costs associated with various aspects of the demonstration were tracked throughout the course of the project. **Table 7.1** summarizes the various cost elements and total cost of the demonstration project. The costs have been grouped by categories as recommended in the Federal Remediation Technologies Roundtable Guide to Documenting Cost and Performance for Remediation Projects (FRTR, 1998). Many of the costs shown on this table are a product of the innovative and technology validation aspects of this project, and would not be applicable to a typical site application. Therefore, a separate "discounted costs" column that excludes or appropriately discounts these costs has been included in **Table 7.1** to provide a cost estimate for implementing this technology at the same scale as the demonstration (i.e., pilot scale).

Costs associated with the *in situ* bioremediation of energetic compounds demonstration at Picatinny Arsenal were tracked from September 2004 until April 2010. The total cost of the demonstration was $737,000, which included $304,200 in capital costs, $154,100 in operation and maintenance (O&M) costs, and $278,700 in demonstration-specific costs (cost related to ESTCP requirements or site selection and characterization). A total of approximately 5,500 cubic yards, or 277,700 gallons (assuming a 25% soil porosity) of contaminated aquifer were treated during the demonstration. This corresponds to a unit cost of approximately $134.00 per cubic yard or $2.65 per gallon of contaminated aquifer (**Table 7.1**). By excluding an estimated $379,900 of research-oriented costs (primarily the costs associated with the installation and sampling of extra monitoring wells, system monitoring equipment used for technology validation, and ESTCP reporting requirements), unit costs are estimated at approximately $65.00 per cubic yard, or $1.29 per gallon of contaminated aquifer for a project of this scale (**Table 7.1**).

For this site, the ability to use a cosubstrate that was readily available in soluble form (such as lactate, citrate or emulsified oil) would have further reduced the cost of remediation by approximately $30,000 to $35,000. This is the estimated cost savings associated with the design, procurement and construction of the system used to mix and inject the cheese whey cosubstrate, as well as the labor required to perform mixing and injection operations. Further, it should be noted that costs associated with an approach that did not involve groundwater recirculation (i.e. direct-push injection or multiple well injections) could be considerably lower, depending on site conditions. However, the success of such treatment approaches would depend extensively on hydrogeologic characteristics and contaminant distribution at the individual site.

Table 7.1
Demonstration Cost Components

Cost Element	Details	Tracked Demonstration Costs	Discounted Costs[1]
CAPITAL COSTS			
Groundwater Modeling	Labor	$3,600	$3,600
System Design	Labor	$37,000	$30,000
Well Installation, Development & Surveying[2]	Labor	$37,200	$24,000
	Materials	$6,100	$4,000
	Subcontracts (driller/surveyor)	$39,700	$25,000
System Installation (electrical service, conex box & PLC, monitoring equipment, cheese whey mixing and injection system, groundwater recirculation system)[3]	Labor	$66,700	$50,000
	Equipment & Materials	$66,000	$48,000
	Subcontracts (electrical, Conex box/PLC)	$41,900	$34,000
Travel		$6,000	$5,000
	Subtotal	**$304,200**	**$223,600**
OPERATION AND MAINTENANCE COSTS			
Groundwater Sampling[3]	Labor	$36,300	$12,000
	Materials	$7,900	$2,500
Analytical	In-House Labor	$12,700	$3,800
	Outside Labs (metals & explosives[2])	$54,100	$12,500
System O&M (including testing & start-up)	Labor	$13,200	$13,200
	Materials (cheese whey, consumables)	$2,700	$2,700
Utilities	Electric	$1,600	$1,600
Reporting & Data Management	Labor	$25,300	$24,000
Travel		$300	$200
	Subtotal	**$154,100**	**$72,500**
OTHER TECHNOLOGY-SPECIFIC COSTS			
Site Selection	Labor & Travel	$5,300	$0
Site Characterization (surface soil investigation, 2 direct-push investigations, installation of 2 monitoring wells, slug tests, pump tests)	Labor (including in-house analytical)	$68,600	$0
	Materials	$12,200	$0
	Subcontractor (driller)	$12,000	$0
Laboratory Microcosm and Column Testing	Labor (including in-house analytical)	$59,500	$20,000
Tracer Testing	Labor (including in-house analytical)	$5,600	$0
	Materials	$300	$0
IPR Meeting & Reporting	Labor & Travel	$27,700	$0
Technology Transfer (presentations, papers)	Labor & Travel	$10,800	$0
Demonstration Plan/Work Plan	Labor	$33,100	$25,000
Final Report	Labor	$24,200	$16,000
Cost and Performance Report	Labor	$19,400	$0
	Subtotal	**$278,700**	**$61,000**
	TOTAL COSTS	**$737,000**	**$357,100**
	ESTIMATED TREATMENT VOLUME (cubic yards)	**5,500**	**5,500**
	ESTIMATED TREATMENT VOLUME (gallons)	**277,700**	**277,700**
	APPROXIMATE TREATMENT COST (per cubic yard)	**$134.00**	**$65.00**
	APPROXIMATE TREATMENT COST (per gallon)	**$2.65**	**$1.29**

Notes:

[1]Discounted costs are defined as estimated costs to implement this technology at the same scale as the demonstration. These costs do not include the technology validation apects of this ESTCP demonstrations, such as site selection, some laboratory testing, tracer testing, extensive groundwater sampling, ESTCP demonstration reporting and meeting (IPR) requirements, and preparation of technical and cost and performance reports.

[2]Includes 2 extraction wells & 1 injection well. Seven additional monitoring wells were installed for demonstration. Three additional monitoring wells assumed for discounted costing.

[3]3 baseline & 10 performance monitoring events were performed during demonstration. A total of five sampling events assumed for discounted costing.

7.1.1 Capital Costs

Capital costs (primarily system design and installation) accounted for $304,200 (or 41 percent) of the total demonstration costs. As indicated in **Table 7.1**, these costs far exceed what would be expected during a typical remediation project due partially to the following unique cost elements:

- The large number of performance monitoring wells (nine) installed within the relatively small (60 x 80') demonstration area.
- The installation of extensive data collection and recording equipment (such as injection and extraction well pressure transducers and related data recording equipment) built into the groundwater recirculation and amendment delivery systems.
- A specially designed mixing tank and pumping system to thoroughly mix the powdered cheese whey into solution. Given that cheese whey addition was required far less frequently than initially expected, a more cost effective approach could be developed, including application of liquid whey.

7.1.2 O&M Costs

O&M costs accounted for $154,100 (or 21 percent) of the total demonstration cost. These costs consisted primarily of groundwater monitoring (including analytical), systems O&M, and reporting costs. System O&M costs (which includes cheese whey material, mixing and injections) were $15,900, or 2 percent of total demonstration costs. The cost of the 2,000 pounds of cheese whey added during the demonstration was less than $1,500 (including freight charges), or 0.2 percent of total demonstration costs. Treatment dosage during the demonstration is estimated at approximately 0.36 lbs. of cheese whey per cubic yard of treated aquifer.

Extensive performance monitoring activities were conducted to effectively validate this technology; including 13 groundwater sampling events (3 baseline, 7 performance, and 3 rebound) and over 750 samples being collected and analyzed over a 23 month period, not including tracer testing (see **Table 5.9**).

7.1.3 Demonstration-Specific Costs

Other demonstration-specific costs (those costs not expected to be incurred during non research-oriented remediation projects) accounted for $278,700 (or 38 percent) of the total demonstration cost. These costs included site selection, laboratory and tracer testing, ESTCP demonstration reporting and meeting (IPR) requirements, and preparation of extensive technical and cost and performance reports.

7.2 Cost Drivers

7.2.1 General Considerations

The expected cost drivers for installation and operation of a semi-passive groundwater recirculation and amendment delivery system for the remediation of explosives contaminated groundwater, and those that will determine the cost/selection of this technology over other options include the following:

- Depth of the plume below ground surface
- Width, length, and thickness of the plume
- Aquifer lithology and hydrogeology
- Regulatory/acceptance of groundwater extraction and re-injection
- Regulatory considerations concerning secondary groundwater impacts (i.e. metals mobilization, sulfate reduction, etc.)
- Length of time for clean-up (e.g., necessity for accelerated clean-up)
- The presence of indigenous bacteria capable of degrading explosive compounds
- Concentrations of contaminants and alternate electron acceptors (e.g., NO_3^-, SO_4^{2-} and O_2)
- Presence of co-contaminants, such as chloroform, chlorinated ethenes, or chlorinated ethanes
- The type(s) of co-substrates determined to be effective at promoting the biodegradation of explosive compounds at a given site (i.e. those that are packaged in soluble form vs. those that need to be mixed into solution prior to injection)
- O&M costs and related issues (particularly injection well fouling)

Another major factor that could potentially lead to significant long-term O&M cost during active *in situ* bioremediation pumping system is well fouling control. During this active treatment project, as well as others that we have recently completed (e.g., Hatzinger and Lippincott, 2009; Hatzinger et al., 2009), control of injection well fouling was a key component of system design and operation. Fouling of wells and other system components during this project was prevented through proper well design, filtration of re-circulated groundwater, and design of the substrate injection program (i.e. high concentrations at low frequency via semi-passive addition). The use of an anti-biofouling agent, such as THPS, on a regular basis also can help to minimize well fouling, although such treatment was not required during this demonstration due to the semi-passive approach employed. This issue remains a critical technical and economic constraint to full-time active pumping designs for *in situ* groundwater treatment using bioremediation (e.g., Hatzinger et al., 2009).

As discussed in detail in Section 5.1, microcosm screening and column treatability testing showed that cheese whey was the most effective cosubstrate (out of the 9 tested) for promoting

biological reduction of RDX, and suggested that this cosubstrate would be effective in the field for HMX as well. Based on the laboratory studies, cheese whey was chosen as the cosubstrate for field injection. Because the cheese whey product used in laboratory tests (see **Figure 5.24**) was packaged in powdered form, dissolution of this cosubstrate in site groundwater in the field was required. Laboratory solubility testing with the cheese whey suggested that a robust mixing system would be required to effectively mix large quantities of the powder into solution. As discussed in Section 7.1, costs associated with the design, procurement and construction of the system used to mix and inject the cheese whey cosubstrate, as well as the labor required to perform mixing and injection operations accounted for a significant portion of the project expenditures. The ability to use a cosubstrate that was readily available in soluble form (such as lactate, acetate, or emulsified vegetable oil [EVO]) would have reduced the cost of remediation significantly. It should be noted that soluble cosubstrates (such as acetate and EVO) have been shown to be effective at treating explosives aquifer materials collected from other sites (e.g., Davis et al., 2004; Schaefer et al., 2007; Kwon et al., 2011), although they were not effective at this location (See Section 5.1).

7.2.2 Competing Treatment Technologies

The three other technologies (in addition to bioremediation using a carbon source such as cheese whey or EVO) that have been proven to treat nitramine and nitroaromatic explosives, such as RDX and TNT in groundwater, to below regulatory levels at the field scale include:

1. Pump and treat (P&T) with carbon treatment
2. Zero valent iron permeable reactive barriers (ZVI PRBs), and
3. Mulch biowalls

Additional technologies, including *in situ* chemical oxidation using permanganate (Albano et al., 2010), an electrolytic barrier (ESTCP Project ER-0519; www.SERDP.org) and *in situ* treatment wells (ISTWs) with granular iron placed outside of the well screens (ESTCP Project ER-0223; www.SERDP.org), have been tested at the field scale, but have failed to consistently reduce concentrations to below regulatory levels of concern.

Pump and Treat technologies provide capture of contaminated groundwater, and above-ground treatment of the extracted water prior to discharge or re-injection into the subsurface. While (if designed properly) these systems can provide protection to downgradient receptors, they are inefficient at removing contaminant mass from a plume and/or source zone, and often require operation for decades, leading to high overall costs.

ZVI PRBs, mulch biowalls, and EVO biobarriers treat contaminated groundwater as it flows through the wall/barrier. While these approaches can provide protection to downgradient receptors, they are even less effective than P&T at removing contaminant mass from the plume and/or source zone. They may also require regular replacement as the materials (ZVI, mulch, or

EVO) are used up or begin to clog, leading to undesired hydraulic conditions (i.e., contaminated groundwater flowing around or beneath the wall/barrier).

As previously discussed, bioremediation approaches can be either "active", where distribution of amendments is achieved using groundwater recirculation, or "passive", where distribution is accomplished during initial injection and/or via ambient groundwater flow (see Stroo and Ward, 2009). Active groundwater treatment approaches often involve pairs or groups of injection and extraction wells to recirculate groundwater and effectively distribute injected amendments within the subsurface. Passive treatment approaches generally involve injection of amendments via closely-spaced injection wells or direct-push technology. A hybrid approach (and the one used during this demonstration) is the "semi-passive" approach, where groundwater is recirculated for a short period to distribute amendments, followed by a longer period of no groundwater recirculation. In each of the above three approaches, a carbon source is typically added in order to promote and maintain the reducing, anoxic conditions and supply carbon needed for *in situ* growth of bacteria capable of degrading target contaminants. A slow-release carbon source, such as EVO is often utilized with passive treatment approaches to reduce injection frequency.

Bioremediation (active, passive, and semi-passive approaches) can be utilized to treat source areas and diffuse plumes, or as a barrier to protect downgradient receptors, whereas the three technologies discussed above (P&T, ZVI PRBs, and mulch biowalls) are primarily used as barriers to protect downgradient receptors. When a bioremediation approach is used to treat contaminated groundwater in the source area and/or throughout the plume, clean-up times associated with this technology are generally substantially shorter than those associated with P&T, ZVI PRBs and mulch biowalls.

The plume characteristics and those of the local aquifer will play an important role in the cost and applicability of the above technologies for remediation of explosives-contaminated groundwater. For shallow groundwater plumes (< 50 ft bgs), passive *in situ* options, such as installation of a PRB consisting of either injection well or direct-push applied slow-release substrates (like EVO), are likely to be a cost effective options, providing the selected substrate(s) have been shown to stimulate indigenous microorganisms capable of degrading target contaminants at the treatment site. Trench installation of mulch biowalls or ZVI PRBs may also provide cost effective options for passively treating contaminants at the downgradient edge of groundwater plumes. These passive systems require little O&M after installation, and have the ability to prevent plumes from spreading or leaving a site. However, they may be less suitable at sites where concerns about secondary groundwater contaminants (e.g. reduction and mobilization of Fe, Mn and As, sulfide from sulfate reduction, etc.) exist. Additionally, trench installed barrier technologies may require replacement (ZVI PRBs) or regular rejuvenation with EVO injections (mulch PRBs) to remain effective.

For deeper plumes (e.g. >50 ft. bgs) or those that are large or very thick, passive approaches are often not technically feasible and/or are cost-prohibitive (e.g., injecting passive substrates at closely spaced intervals to > 50 ft bgs). Active or semi-passive treatment systems may be technically and economically more attractive under these conditions. Active or semi-passive treatment approaches may also be better suited for heterogeneous geologies or sites where pH adjustment is required, as groundwater recirculation improves mixing and distribution of injected amendments within the subsurface. Longer treatment time frames, high contaminant concentrations, and secondary reaction concerns may also present conditions favorable for utilizing an active approach, since amendment addition and mixing rates can be adjusted more easily then with passive approaches (which often utilize less frequent injection of amendments at high concentrations). However, these approaches may be limited where re-injection of contaminated water (e.g., extracted groundwater with amendments) is either prohibited due to water usage/rights concerns or subject to regulatory injection permits.

7.3 Cost Analysis

A thorough cost analysis of various *in situ* treatment approaches, including active-pumping systems, passive systems, and semi-passive designs is provided in *In Situ Bioremediation of Perchlorate in Groundwater* (Chapter 10; Krug et al., 2009). These approaches are compared technically and economically with each other and with *ex situ* treatment under a variety of different contamination scenarios. The reader is referred to this chapter and others in this volume for descriptions and economic comparisons of different *in situ* technologies that have shown to be capable of remediating perchlorate in groundwater. The base case and cost analysis presented in this book were used as a template for the cost analysis of the technology tested during this demonstration, as well as the other technologies discussed above that have been proven effective at treating explosives contaminated groundwater. A cost analysis for the base case was performed for the following technologies:

1. Semi-passive bioremediation of the entire plume using cheese whey
2. Semi-passive biobarrier using cheese whey
3. Passive injection biobarrier with EVO
4. Passive trench mulch biowall
5. Passive trench ZVI PRB
6. Pump and treat

Because of the limited applicability of these other treatment technologies (i.e. limited to barrier applications and/or limited depths), semi-passive bioremediation of the entire plume cannot be directly compared to the other technologies. Therefore, cost analyses comparing the above approaches are presented based on a 30-year operating scenario.

7.3.1 Base Case Template

As discussed above, the base case presented in Krug et al., (2009) is used as a template for the cost analysis of the above technologies/approaches. In the current scenario, however, TNT and RDX are substituted for perchlorate as the contaminant(s) of concern. The base case presents a situation where a shallow aquifer, consisting of homogeneous silty sands, is contaminated with TNT and RDX. The explosives-impacted groundwater extends from 10 to 40 feet bgs, along the direction of groundwater flow for 800 feet, and is 400 feet in width (**Figure 7.1**). The specific base case site characteristics, including aquifer characteristics and design parameters for each of the remedial approaches analyzed are summarized in **Table 7.2**. The costing for the template site assumes that the source zone has been treated, and that that there is no continuing source of groundwater contamination.

As indicated in **Table 7.2**, the base case assumes a groundwater seepage velocity of approximately 33 ft/year, and that two pore volumes of clean water will need to flush through the impacted area to achieve the cleanup objectives. However, as stated in Krug et al., (2009), there are a number of factors, such as the degree of heterogeneity of the geological media, that will determine the actual number of pore volumes of clean water required to flush through the subsurface to achieve target treatment objectives. Variations in the hydraulic conductivity (K) of the aquifer materials can allow a significant fraction of the total mass of contaminants to diffuse into low K layers, and then act as an ongoing source to the higher K zones. In most geological settings, it is likely that more than two pore volumes would be required to achieve treatment objectives, thus leading to longer treatment times (and costs) for passive and P&T approaches.

The following subsections provide cost estimates for implementation of each the six treatment approaches for the base case. The cost estimates provide insight into the comparative capital, O&M, and long term monitoring costs to better identify cost drivers for each technology/ approach. Total costs and the Net Present Value (NPV) of future costs were calculated for each of treatment approaches. Future costs (O&M and long term monitoring costs) are discounted, using a 2% discount rate, to determine the NPV estimates of these costs (OMB, 2012). Specifically excluded from consideration are the costs of pre-remedial investigations and treatability studies, assuming the costs for these activities would be similar for each alternative.

Table 7.2
Summary of Base Case Site Characteristics and Design Parameters for Treatment of Explosives-Impacted Groundwater

Design Parameter	Units	Alternative					
		Active Plume Treatment (Whey)	Semi-Passive Biobarrier (Whey)	Passive Injection Biobarrier (EVO)	Passive Trench Mulch Biowall	Passive Trench ZVI PRB	Pump and Treat
Width of Plume	feet	400	400	400	400	400	400
Length of Plume	feet	800	800	800	800	800	800
Depth to Water	feet	10	10	10	10	10	10
Vertical Saturated Thickness	feet	40	40	40	40	40	40
Porosity	dimensionless	0.25	0.25	0.25	0.25	0.25	0.25
Gradient	dimensionless	0.008	0.008	0.008	0.008	0.008	0.008
Hydraulic Conductivity	ft/day	2.8	2.8	2.8	2.8	2.8	2.8
Groundwater Seepage Velocity	ft/year	33	33	33	33	33	33
Upgradient Combined TNT & RDX Concentration	µg/L	2,000	2,000	2,000	2,000	2,000	2,000
Downgradient Combined TNT & RDX Concentration	µg/L	10	10	10	10	10	10
Nitrate Concentration	mg/L	15	15	15	15	15	15
Dissolved Oxygen Concentration	mg/L	5	5	5	5	5	5
TNT Treatment Objective	µg/L	2	2	2	2	2	2
RDX Treatment Objective	µg/L	2	2	2	2	2	2
Assumed Number of Pore Volumes to Flush Plume	each	2	2	2	2	2	2
Number of Barriers	each	NA	1	1	1	1	NA
Number of Monitoring Wells	each	10	10	10	10	10	10
Number of Amendment Injection Wells	each	0	0	30	20	0	0
Number of Groundwater Extraction Wells	each	64	4	0	0	0	4
Number of Groundwater Re-Injection Wells	each	72	5	0	0	0	0
Groundwater Travel Time to Barrier	years	NA	24	24	24	24	NA
Years to Clean Up Groundwater	years	3	48	48	48	48	NA

NA - Not Applicable

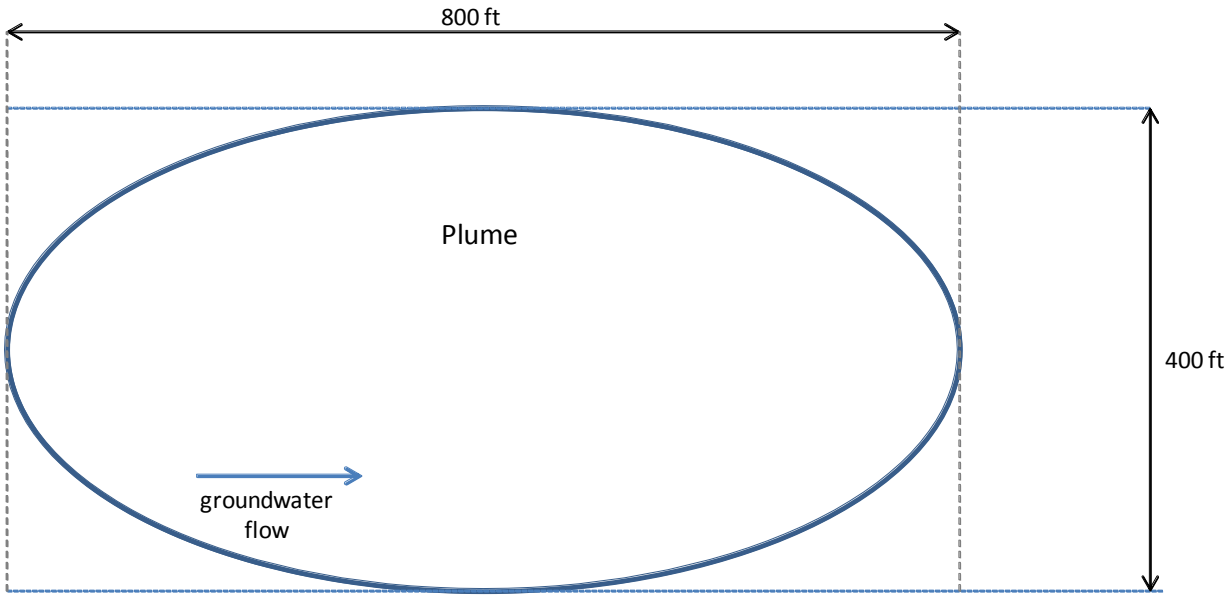


Figure 7.1. Base case plume characteristics (modified from Krug et al., 2009).

7.3.2 Semi-Passive Bioremediation of the Entire Plume

The semi-passive bioremediation alternative assumes that a series of alternating rows of injection and extraction wells are installed throughout the entire 320,000 square foot plume to recirculate groundwater and distribute cheese whey as a cosubstrate for explosives bioremediation. As shown in **Figure 7.2**, well and row spacing is 50 feet, with 8 rows of 9 injection wells, and 8 rows of 8 extraction wells, for a total of 136 wells. Groundwater will be recirculated between the rows of wells, and cheese whey added for approximately 3 weeks, after which the system will be shut down for a period of 9 months. Treatment will occur at one-quarter of the wells at a time (rows 1 through 4, followed by rows 5 through 8, etc.) to minimize the size of the groundwater recirculation and cheese whey mixing systems, and the number of submersible groundwater extraction pumps and associated equipment required. Treatment will be performed three times over the first three years of the project, providing greater than 2½ years of continued treatment of the contaminated aquifer (almost twice as long as the treatment period that was shown to be successful during the demonstration). This alternative also assumes no O&M costs after year 3, and no long term monitoring costs after year 20.

As summarized in **Table 7.3**, the estimated total costs for this alternative over 20 years are $1,950,000 with a total NPV of lifetime costs of $1,890,000. The capital cost including design, work plan, installation of recirculation and monitoring wells, construction of the groundwater recirculation and cheese whey mixing systems, and system start up and testing are approximately $1,140,000. Approximately two-thirds of these costs (approximately $710,000) are associated with installation of the groundwater recirculation and monitoring wells. The NPV of the O&M is estimated at approximately $430,000 for the first three years of treatment. The O&M costs include the labor costs associated with three rounds (12 weeks each) of cheese whey mixing and injection, labor for system O&M, costs for equipment repair and replacement, and cost for the cheese whey. The NPV of the 20 years of monitoring and reporting costs is estimated to be $320,000.

While this alternative has the lowest estimated total remedy cost of the 6 alternatives analyzed, the NPV of lifetime costs ranks 3rd at $1,890,000 (see **Table 7.9**). This is primarily due to the high capital costs incurred during the first year of implementing this technology. As discussed below, while the other alternatives may have higher O&M and monitoring costs, these costs are spread out over 30 years, and the 2% discount rate used in the NPV estimates decreases the effect of longer term costs on the NPV of lifetime costs. However, it should be noted that should the passive treatment technologies require more than 30 years of implementation to achieve site objectives (which is likely), then additional O&M and long term monitoring costs for these alternatives could easily make the NPV of lifetime costs higher than this alternative. Additionally, it is also likely that long term monitoring costs (currently 20 years) could be reduced for this alternative, if successful remediation leads to reduced monitoring frequency and

duration. In many cases, the accelerated cleanup (3 years vs. 30+ years), and reduction in long-term liability will be worth slightly higher lifetime costs.

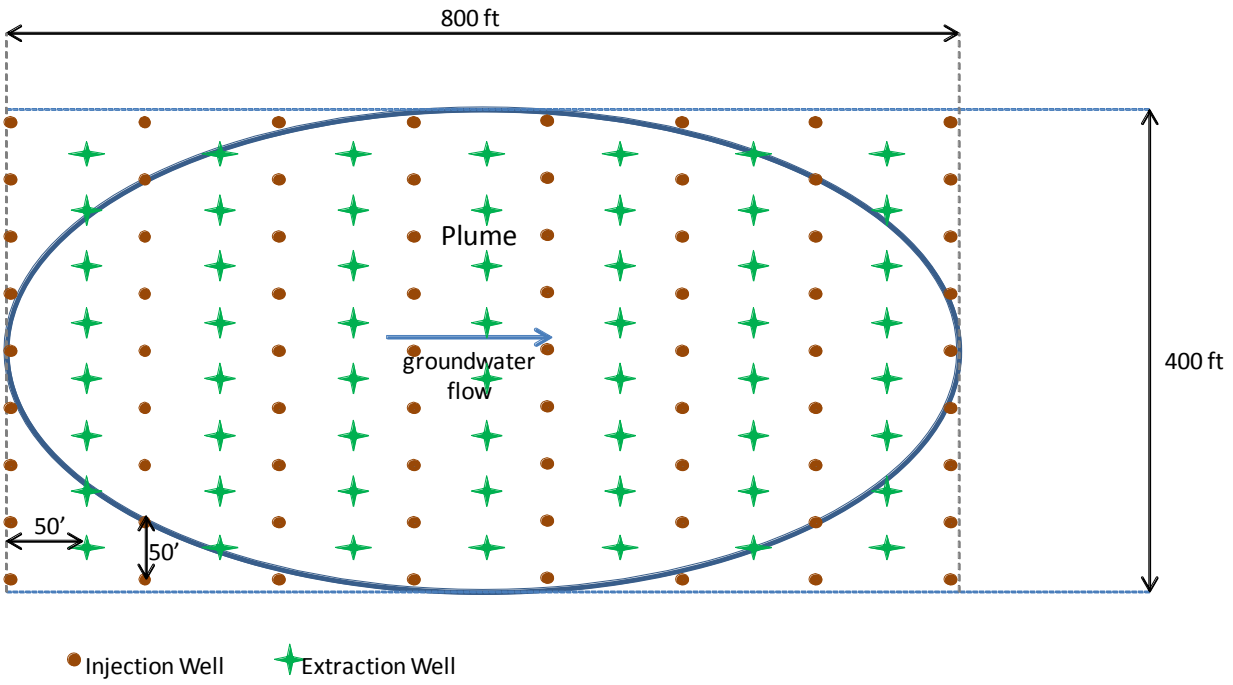


Figure 7.2. Semi-passive bioremediation alternative with cheese whey for whole plume treatment.

Table 7.3. Cost Components for Semi-Passive Bioremediation of an Explosives-Impacted Groundwater Plume

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5	6	7 to 20		
CAPITAL COSTS									
System Design	95,142	-	-	-	-	-		95,142	95,142
Well Installation	709,662	-	-	-	-	-		709,662	709,662
System Installation	331,417	-	-	-	-	-		331,417	331,417
Start-up and Testing	5,040	-	-	-	-	-		5,040	5,040
SUBCOST ($)	1,141,261	-	-	-	-	-		**1,141,261**	**1,141,261**
OPERATION AND MAINTENANCE COSTS									
System Operation and Maintenance	144,888	144,888	144,888	-	-	-		426,198	434,665
SUBCOST ($)	**144,888**	**144,888**	**144,888**	-	-	-		**426,198**	**434,665**
LONG TERM MONITORING COSTS									
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	37,002	37,002	37,002	37,002	37,002	12,369	12,369 every year	324,725	370,545
SUBCOST ($)	**37,002**	**37,002**	**37,002**	**37,002**	**37,002**	**12,369**		**324,725**	**370,545**
TOTAL COST ($)	**1,323,151**	**181,890**	**181,890**	**37,002**	**37,002**	**12,369**		**1,892,184**	**1,946,471**

NPV - Net Present Value

* - NPV calculated based on a 2% discount rate

7.3.3 Semi-Passive Biobarrier

The semi-passive biobiarrier alternative assumes that a series of four extraction and five injection wells will be installed at the downgradient edge and perpendicular to the axis of the plume (**Figure 7.3**). Groundwater will be recirculated between the rows of wells, and cheese whey added for approximately 3 weeks, after which time the system will be shut down for a period of 9 months. The biobarrier will be operated in this semi-passive mode for a period of 30 years. This alternative also assumes 30 years of associated O&M and long term monitoring costs.

As summarized in **Table 7.4**, the estimated total costs for this alternative over 30 years are $2,240,000 with a total NPV of lifetime costs of $1,840,000. The capital cost including design, work plan, installation of recirculation and monitoring wells, construction of the groundwater recirculation and cheese whey mixing systems, and system start up and testing are approximately $460,000. The NPV of the O&M is estimated at approximately $980,000 for the 30 years of treatment. The O&M costs include the labor costs associated with regular rounds (every 9-10 months) of cheese whey mixing and injection, labor for system O&M, costs for equipment repair and replacement, and cost for the cheese whey. The NPV of the 30 years of monitoring and reporting costs is estimated to be $400,000.

This alternative ranks third in estimated total remedy cost and second in NPV of lifetime costs (see **Table 7.9**). While this technology has relatively modest estimated capital costs, the long term O&M costs make it less attractive, especially if the system needs to operate beyond 30 years.

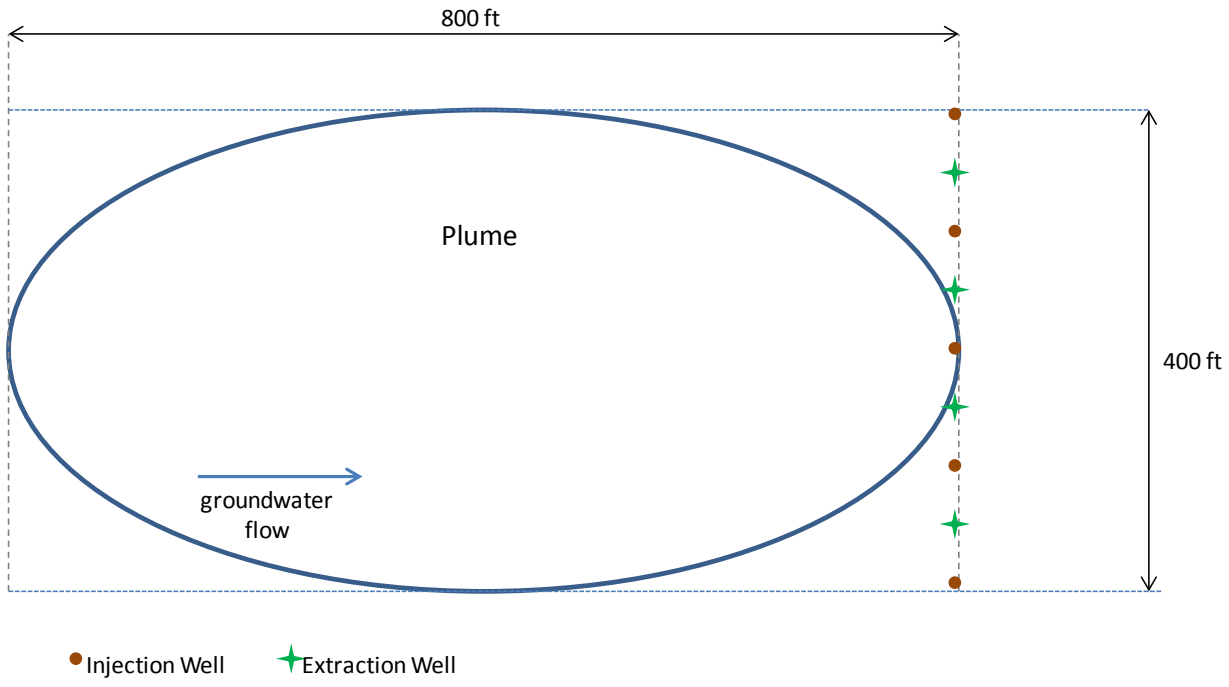


Figure 7.3. Semi-passive biobarrier alternative with cheese whey for plume cutoff.

Table 7.4. Cost Components for Semi-Passive Biobarrier Treatment of Explosives-Impacted Groundwater

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5	6	7 to 30		
CAPITAL COSTS									
System Design	95,142	-	-	-	-	-		95,142	95,142
Well Installation	80,738	-	-	-	-	-		80,738	80,738
System Installation	265,980	-	-	-	-	-		265,980	265,980
Start-up and Testing	17,978	-	-	-	-	-		17,978	17,978
SUBCOST ($)	459,838	-	-	-	-	-		**459,838**	**459,838**
OPERATION AND MAINTENANCE COSTS									
System Operation and Maintenance	27,732	43,482	43,482	43,482	43,482	43,482	42,482 every year	977,580	1,288,724
SUBCOST ($)	**27,732**	**43,482**	**43,482**	**43,482**	**43,482**	**43,482**		**977,580**	**1,288,724**
LONG TERM MONITORING COSTS									
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	37,002	37,002	37,002	37,002	37,002	12,369	12,369 every year	400,991	494,235
SUBCOST ($)	**37,002**	**37,002**	**37,002**	**37,002**	**37,002**	**12,369**		**400,991**	**494,235**
TOTAL COST ($)	**524,572**	**80,484**	**80,484**	**80,484**	**80,484**	**55,851**		**1,838,409**	**2,242,796**

Notes:
NPV - Net Present Value
* - NPV calculated based on a 2% discount rate

7.3.4 Passive Injection Biobarrier

The passive injection biobarrier alternative assumes that a series of 30 injection wells will be installed at the downgradient edge and perpendicular to the axis of the plume (**Figure 7.4**). An initial injection during year 1, and reinjection of EVO every 3 years after, will be performed to create a passive biobarrier. The biobarrier will be maintained for a period of 30 years. This alternative also assumes 30 years of associated O&M and long term monitoring costs.

As summarized in **Table 7.5**, the estimated total costs for this alternative over 30 years are $2,390,000 with a total NPV of lifetime costs of $1,910,000. The capital cost including design, work plan, installation of injection and monitoring wells, and the initial EVO injection are approximately $320,000. The NPV of the O&M is estimated at approximately $1,180,000 for the 30 years of treatment. The O&M costs primarily include the labor and material costs associated with regular injections (every 3 years) of EVO. The NPV of the 30 years of monitoring and reporting costs is estimated to be $400,000.

This alternative ranks fifth in estimated total remedy cost and fourth in NPV of lifetime costs (see **Table 7.9**). The estimated capital costs for this approach are the lowest of the six alternatives because of the limited infrastructure required. However, the long term O&M costs associated with regular injections of EVO make this one of the more expensive alternatives, with total remedy costs second only to the pump and treat alternative. As with the other barrier approaches (including pump and treat), total remedy costs will increase if the treatment needs to extend beyond 30 years.

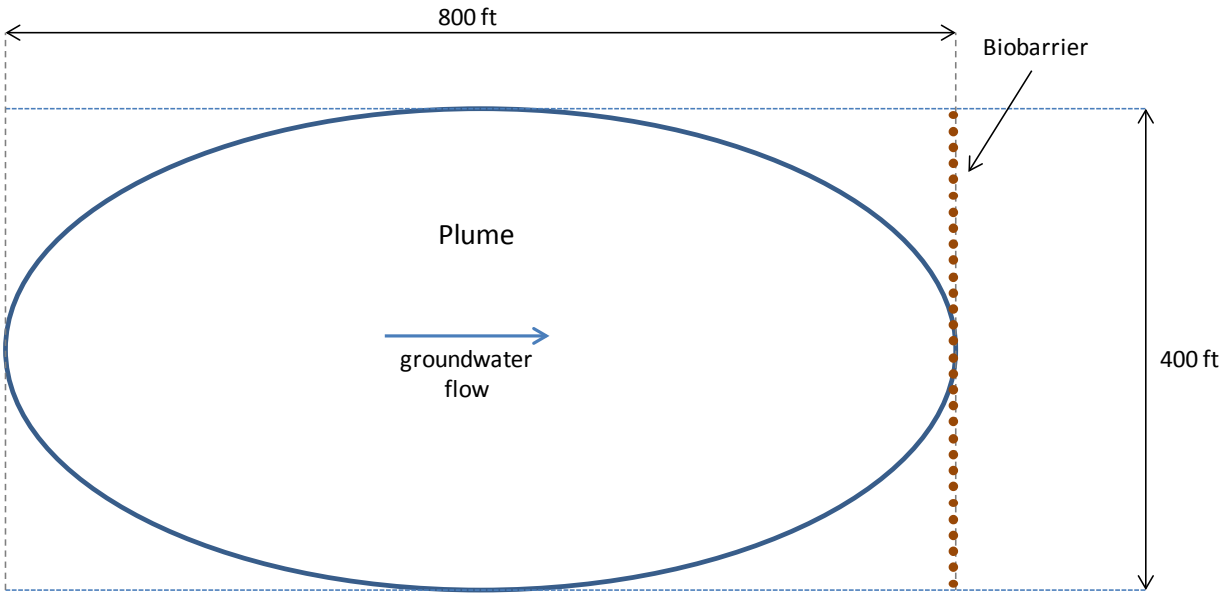


Figure 7.4. Passive biobarrier alternative with EVO for plume cutoff.

Table 7.5. Cost Components for Passive Injection Biobarrier Treatment of Explosives-Impacted Groundwater

	Year Cost is Incurred								NPV of Costs*	Total Costs
	1	2	3	4	5	6	7	8 to 30		
CAPITAL COSTS										
System Design	71,505	-	-	-	-	-	-	-	71,505	71,505
Well Installation (30 1" PVC Wells)	67,393	-	-	-	-	-	-	-	67,393	67,393
Substrate Injection	184,573	-	-	-	-	-	-	-	184,573	184,573
Start-up and Testing**	-	-	-	-	-	-	-	-	0	0
SUBCOST ($)	323,471	-	-	-	-	-	-	-	**323,471**	**323,471**
OPERATION AND MAINTENANCE COSTS										
Substrate Injection	-	-	-	174,598	-	-	174,598	174,598 every 3 years	1,181,345	1,571,384
SUBCOST ($)	-	-	-	**174,598**	-	-	**174,598**		**1,181,345**	**1,571,384**
LONG TERM MONITORING COSTS										
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	37,002	37,002	37,002	37,002	37,002	12,369	12,369	12,369 every year	400,991	494,235
SUBCOST ($)	**37,002**	**37,002**	**37,002**	**37,002**	**37,002**	**12,369**	**12,369**		**400,991**	**494,235**
TOTAL COST ($)	**360,473**	**37,002**	**37,002**	**211,600**	**37,002**	**12,369**	**186,967**		**1,905,807**	**2,389,090**

Notes:

NPV - Net Present Value

* - NPV calculated based on a 2% discount rate

** - No "Start-up and Testing" costs are included because no operating equipment is left behind following substrate injection

7.3.5 Passive Trench Mulch Biowall

The passive trench mulch biowall alternative assumes an initial installation of a mulch biowall in a trench at the downgradient edge and perpendicular to the axis of the plume (**Figure 7.5**). The mulch biowall will be installed using the one-pass trenching/installation method, and will be 400 feet long, 2 feet thick, and extend down to 40 feet bgs. The biowall will be rejuvenated 4 and 8 years after installation, and then every 3 years thereafter by injecting EVO into 20 injection wells installed within the mulch biowall. The EVO injections are required because the organics in the mulch will eventually be depleted. The biowall will be maintained for a period of 30 years. This alternative also assumes 30 years of associated O&M and long term monitoring costs.

As summarized in **Table 7.6**, the estimated total costs for this alternative over 30 years are $2,170,000 with a total NPV of lifetime costs of $1,710,000. The capital cost including design, work plan, mulch biowall installation, and installation of injection and monitoring wells are approximately $360,000. The NPV of the O&M is estimated at approximately $950,000 for the 30 years of treatment. The O&M costs primarily include the labor and material costs associated with injections of EVO to maintain the biowall. The NPV of the 30 years of monitoring and reporting costs is estimated to be $400,000.

This alternative ranks second in estimated total remedy cost and lowest in NPV of lifetime costs (see **Table 7.9**). The estimated capital costs for this approach are higher than those of the passive injection biobarrier, because of the higher costs associated with the construction of the trench biowall relative to the costs for the initial injection of EVO. However, the long term O&M costs associated with maintaining the mulch biowall are less than those of the passive injection biobarrier, because less frequent injections (and less quantity) of EVO will be required to maintain the mulch biowall, relative to the passive injection biobarrier. As with the other barrier approaches (including pump and treat), total remedy costs will increase if the treatment extends beyond 30 years.

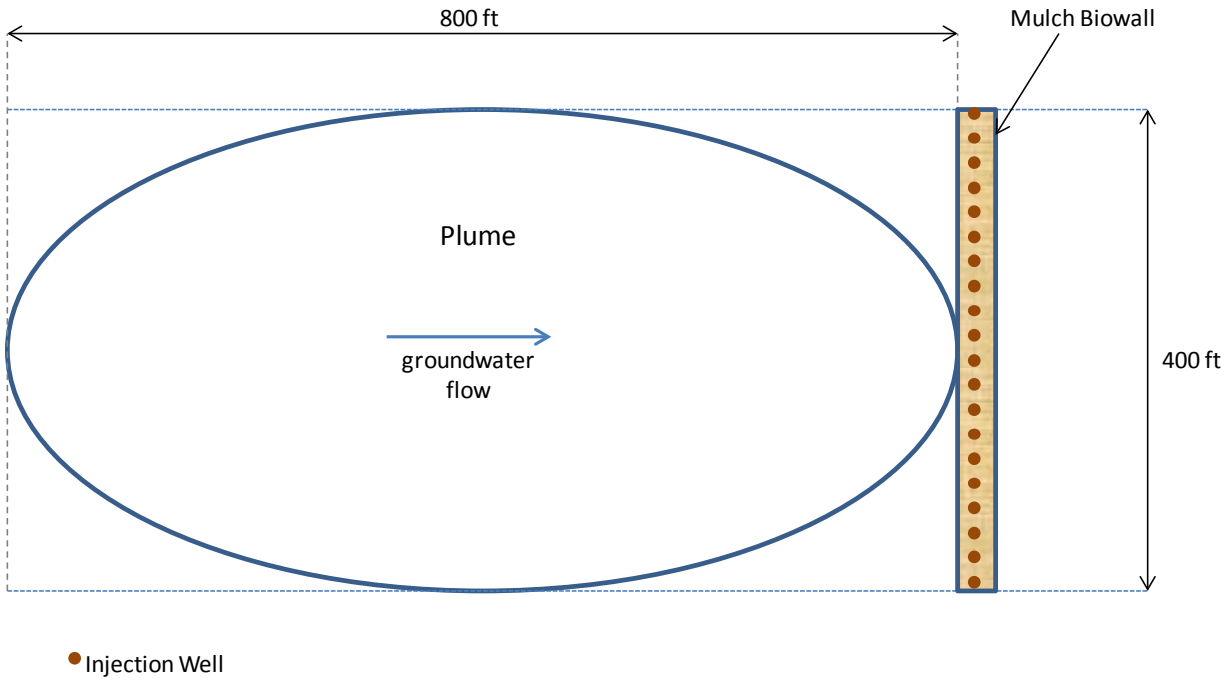


Figure 7.5. Passive biobarrier alternative utilizing a mulch wall for plume cutoff.

Table 7.6. Cost Components for Passive Trench Biowall Treatment of Explosives-Impacted Groundwater

	Year Cost is Incurred									NPV of Costs*	Total Costs
	1	2	3	4	5	6	7	8	9 to 30		
CAPITAL COSTS											
System Design	65,205	-	-	-	-	-	-	-		65,205	65,205
Well Installation	53,064	-	-	-	-	-	-	-		53,064	53,064
Trench Installation	191,013	-	-	-	-	-	-	-		191,013	191,013
Substrate Injection	52,500	-	-	-	-	-	-	-		52,500	52,500
Start-up and Testing**	-	-	-	-	-	-	-	-		0	0
SUBCOST ($)	361,782	-	-	-	-	-	-	-		**361,782**	**361,782**
OPERATION AND MAINTENANCE/REAPPLICATION COSTS	-	-	-	145,968	-	-	-	145,968	145,968 every 3 years	957,111	1,313,711
SUBCOST ($)	-	-	-	**145,968**	-	-	-	**145,968**		**957,111**	**1,313,711**
LONG TERM MONITORING COSTS											
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	37,002	37,002	37,002	37,002	37,002	12,369	12,369	12,369	12,369 every year	400,991	494,235
SUBCOST ($)	37,002	37,002	37,002	37,002	37,002	12,369	12,369	12,369		**400,991**	**494,235**
TOTAL COST ($)	**398,784**	**37,002**	**37,002**	**182,970**	**37,002**	**12,369**	**12,369**	**158,337**		**1,719,884**	**2,169,728**

Notes:

NPV - Net Present Value

* - NPV calculated based on a 2% discount rate

** - No "Start-up and Testing" costs are included because no operating equipment is left behind following substrate injection

7.3.6 Passive Trench ZVI PRB

The passive trench ZVI PRB alternative assumes an initial installation of a ZVI PRB in a trench at the downgradient edge and perpendicular to the axis of the plume (**Figure 7-1e**). The PRB will consist of 25% ZVI filings and 75% coarse sand fill mixture (v/v). Like the passive mulch biowall, the PRB will be installed using the one-pass trenching/installation method, and will be 400 feet long, 2 feet thick, and extend down to 40 feet bgs. Pricing for this alternative assumes the PRB will need to be replaced after 15 years, due to decline in ZVI reactivity and/or plugging. The PRB will be maintained for a period of 30 years. This alternative also assumes 30 years of associate O&M and long term monitoring costs.

As summarized in Table 7.7, the estimated total costs for this alternative over 30 years are $2,270,000 with a total NPV of lifetime costs of $1,970,000. The capital cost including design, work plan, ZVI PRB installation, and installation of monitoring wells are approximately $940,000. The NPV of the O&M is estimated at approximately $640,000, which is the NPV associated with the replacement of the PRB after 15 years. The NPV of the 30 years of monitoring and reporting costs is estimated to be $400,000.

This alternative ranks fourth in estimated total remedy cost and fifth in NPV of lifetime costs (Table 7.9). The estimated capital costs for this approach are higher than those of the passive trench mulch biowall, because of the much higher costs associated with ZVI PRB material relative to the costs for the mulch biowall material. However, the long term O&M costs associated with maintaining the ZVI PRB are less than those of the mulch biowall, because no injections are required to maintain the mulch biowall. The total remedy costs for this alternative would increase significantly if the PRB lifespan was less than 15 years, or if treatment extended beyond 30 years.

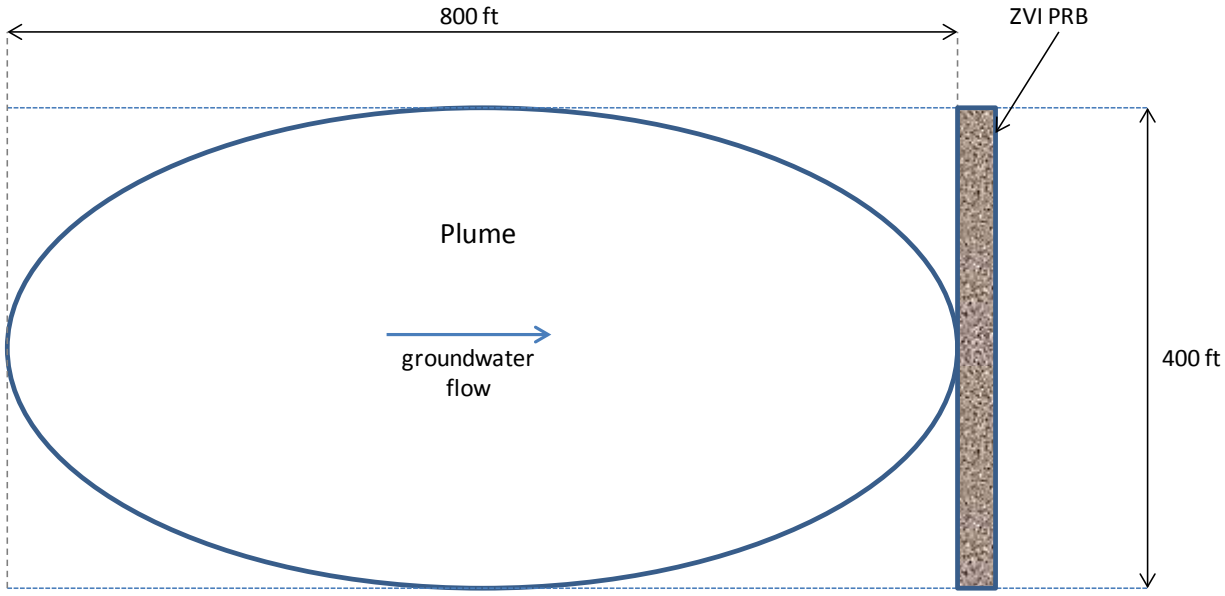


Figure 7.6. Passive barrier alternative utilizing ZVI for plume cutoff.

Table 7.7. Cost Components for Passive Trench ZVI PRB Treatment of Explosives-Impacted Groundwater

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5 to 14	15	16 to 30		
CAPITAL COSTS									
System Design	65,205	-	-	-		-		65,205	65,205
Well Installation	29,084	-	-	-		-		29,084	29,084
Trench Installation	191,013	-	-	-		-		191,013	191,013
PRB Material	650,000	-	-	-		-		650,000	650,000
Start-up and Testing**	-	-	-	-		-		0	0
SUBCOST ($)	935,302	-	-	-		-		**935,302**	**935,302**
OPERATION AND MAINTENANCE/REAPPLICATION COSTS									
PRB Replacement Cost	-	-	-	-		841,013		637,383	841,013
SUBCOST ($)	-	-	-	-		**841,013**		**637,383**	**841,013**
LONG TERM MONITORING COSTS									
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	37,002	37,002	37,002	37,002	12,369 every year	12,369	12,369 every year	400,991	494,235
SUBCOST ($)	37,002	37,002	37,002	37,002		12,369		**400,991**	**494,235**
TOTAL COST ($)	**972,304**	**37,002**	**37,002**	**37,002**		**853,382**		**1,973,675**	**2,270,550**

Notes:

NPV - Net Present Value

* - NPV calculated based on a 2% discount rate

** - No "Start-up and Testing" costs are included because no operating equipment is left behind following substrate injection

7.3.7 Pump and Treat

The groundwater extraction and treatment (pump and treat) system alternative would be similar to the semi-passive biobarrier system, in that a row of four extraction and five injection wells would be used to recirculate groundwater at the downgradient edge and perpendicular to the axis of the plume (**Figure 7.3**). However, in this case, the extracted groundwater would be treated above ground by passing it through granular activated carbon (GAC), and the treated groundwater re-injected (providing hydraulic control and mass removal at the downgradient edge of the plume). The pump and treat system will be maintained for a period of 30 years. This alternative also assumes 30 years of associated O&M and long term monitoring costs.

As summarized in **Table 7.8**, the estimated total costs for this alternative over 30 years are $3,340,000 with a total NPV of lifetime costs of $2,690,000. The capital cost including design, work plan, installation of extraction/injection and monitoring wells, construction of the groundwater treatment system, and system start up and testing are approximately $510,000. The NPV of the O&M is estimated at approximately $1,780,000. The O&M costs include the labor costs associated with system O&M, costs for equipment repair and replacement, electrical costs,

and cost for the replacement and disposal of the GAC. The NPV of the 30 years of monitoring and reporting costs is estimated to be $400,000.

This alternative ranks last in both estimated total remedy cost and NPV of lifetime costs (**Table 7.9**). The estimated capital costs for this alternative are higher than those of the semi-passive alternative because of the higher costs associated with constructing a groundwater treatment system, compared to constructing a whey mixing system. The high O&M costs associated with operating the pump and treat system are what makes this alternative the least attractive of the six alternatives. As with the other barrier approaches, total remedy costs will increase if the treatment needs to extend beyond 30 years.

Table 7.8. Cost Components for Extraction and Treatment of Explosives-Impacted Groundwater

	Year Cost is Incurred							NPV of Costs*	Total Costs
	1	2	3	4	5	6	7 to 30		
CAPITAL COSTS									
System Design	95,142	-	-	-	-	-		95,142	95,142
Well Installation	80,738	-	-	-	-	-		80,738	80,738
System Installation	306,980	-	-	-	-	-		306,980	306,980
Start-up and Testing	26,250	-	-	-	-	-		26,250	26,250
SUBCOST ($)	509,110	-	-	-	-	-		**509,110**	**509,110**
OPERATION AND MAINTENANCE COSTS									
System Operation and Maintenance	55,809	82,059	82,059	82,059	82,059	82,059	82,059 every year	1,781,478	2,339,834
SUBCOST ($)	**55,809**	**82,059**	**82,059**	**82,059**	**82,059**	**82,059**		**1,781,478**	**2,339,834**
LONG TERM MONITORING COSTS									
Sampling/Analysis/Reporting (Quarterly through 5 years then Annually)	37,002	37,002	37,002	37,002	37,002	12,369	12,369 every year	400,991	494,235
SUBCOST ($)	**37,002**	**37,002**	**37,002**	**37,002**	**37,002**	**12,369**		**400,991**	**494,235**
TOTAL COST ($)	**601,921**	**119,061**	**119,061**	**119,061**	**119,061**	**94,428**		**2,691,578**	**3,343,178**

Notes:
NPV - Net Present Value
* - NPV calculated based on a 2% discount rate

Table 7.9.
Summary of Capital Costs and NPV of Costs for O&M and Monitoring for Treatment of Explosives-Impacted Groundwater

Alternative	Capital Costs	NPV of 30 Years of O&M Costs	NPV of 30 Years of Monitoring Costs	NPV of 30 Years of Total Remedy Costs	Total 30-Year Remedy Costs
Active Plume Treatment (whey)	$1,140	$430	$320	$1,890	$1,950
Semi-Passive Biobarrier (whey)	$460	$980	$400	$1,840	$2,240
Passive Injection Biobarrier (EVO)	$320	$1,180	$400	$1,910	$2,390
Passive Trench Biowall	$360	$960	$400	$1,720	$2,170
Passive Trench ZVI PRB	$940	$640	$400	$1,970	$2,270
Pump and Treat	$510	$1,780	$400	$2,690	$3,340

notes: All costs are in thousands of dollars
NPV - Net Present Value; current value of future costs based on a 2% annual discount rate
O&M - Operation and Maintenance

8.0 Implementation Issues

8.1 End-User Issues

The primary end-users of this technology are expected to be DoD site managers and their contractors, consultants and engineers. The general concerns of these end users are likely to include the following: (1) technology applicability and performance under local site conditions; (2) technology scale-up; (3) secondary impacts to the local aquifer; and (4) technology cost compared to other remedial options. These implementation issues are addressed in the following sections.

8.1.1 Technology Applicability and Performance under Local Site Conditions

The technology utilized during this demonstration was the injection of a cosubstrate through semi-passive pumping. This approach is both highly flexible and widely applicable under differing aquifer conditions. The development of a semi-passive approach for groundwater treatment has evolved in large part from operational issues associated with full-time active pumping systems for *in situ* treatment, and in particular, well biofouling issues. A full-time active pumping system is perhaps the best way to effectively inject and mix substrates into groundwater, in addition to providing hydraulic control at a site. However, technical and cost issues associated with biofouling of injection wells in active systems remain a significant detriment to the widespread application of this approach. The semi-passive treatment approach provides many of the benefits of full-time active treatment, including effective distribution of a soluble carbon source and flexibility in design and operation, but has less overall potential for biofouling due to the limited time of operation of the extraction and reinjection wells. A number of different pilot and full-scale systems have successfully employed a semi-passive remedial design for substrate addition as described previously in Section 2.2 (see also Devlin and Barker, 1994; Devlin and Barker, 1999; Devlin et al. 2004; Gierczak et al., 2007; Hatzinger and Lippincott, 2009; Krug and Cox, 2009; Hyndman et al., 2000). This approach can also be used cost-effectively in deep as well as shallow aquifers and to aerially wide plumes. Aquifer depth is one of the limiting factors for fully passive designs, which become increasingly expensive due to close spacing of injection points and/or technically impractical (e.g., for passive trench barriers) as the depth to the water table increases (Stroo and Ward, 2009). A semi-passive pumping design has fewer limitations with depth. Similarly, wide plumes are more readily treated with active or semi-passive approaches than with fully passive designs as a few wells (and high flow rates) can often be used to distribute cosubstrate over a large area rather than closely spaced wells or injection points [see Stroo and Ward (2009) for further comparisons of different amendment designs].

The primary issues with applying semi-passive cosubstrate addition as a remedial approach are (1) designing the system based on the local hydrogeology and plume characteristics to optimize substrate distribution; (2) operating the system to minimize O&M; and (3) choosing the most effective cosubstrate to promote contaminant biodegradation. As with any *in situ* system, it is

critical to have a good understanding of the plume characteristics and hydrogeology of the region requiring treatment. The semi-passive design is flexible with respect to extraction and injection well numbers, well placement, and flow rates, and various designs have been utilized including several alternating extraction and injection wells as a cutoff barrier (e.g., Krug and Cox, 2009), or only two extraction wells and a single injection well, as was employed in this demonstration for source area treatment and at the former Whittaker-Bermite site for perchlorate (Hatzinger and Lippincott, 2009).

Extensive site assessment work was conducted during this demonstration as well as the others cited above in order to determine the extent of contamination in groundwater (Hydropunch, well installation and baseline sampling over time) and the groundwater hydrology, including aquifer storativity, hydraulic conductivity, and the groundwater flow rate and direction (slug tests, pump tests, groundwater elevation measurements on multiple occasions). In addition, treatability studies were conducted to evaluate the most effective cosubstrates to promote explosives biodegradation in the local aquifer, as the literature has shown that many different soluble carbon sources may be applicable at specific sites (see Section 1.1). Degradation rates for key explosives were then determined for the various cosubstrates and a choice was made based upon effectiveness and cost. All of the site data was subsequently incorporated into a model and simulations were conducted to determine the zone of influence and to evaluate the influence of modifying flow rates and pumping cycles. This basic site assessment and treatability study approach employed during this demonstration is routinely used to determine the most effective technologies for site clean-up, and is recommended for implementing a semi-passive treatment approach for explosives at small or large scale. Groundwater modeling is a critical component of this approach (and nearly any other *in situ* system) because it allows educated decisions on system design (well placement and screening, flow rates) and provides a basis for evaluating operational data and making operational changes.

The cosubstrate utilized during this demonstration (a powdered cheese whey feed additive; **Figure 5.24**) was dictated by treatability study results. Among nine different cosubstrates tested (acetate, lactate, benzoate, hydrogen gas, citrate, ethanol, glucose, yeast extract, and cheese whey) only the cheese whey and yeast extract effectively promoted biodegradation of RDX, HMX, and TNT. Between these two cosubstrates, biodegradation rates were higher for both RDX and HMX using the powdered whey compared to yeast extract (Section 5.1.2). The reason for the high substrate selectivity at Picatinny Area 157 is unclear, and may reflect either the groundwater geochemistry or the explosives degrading microbial community. Although effective, the powdered whey product was difficult to apply to the aquifer at large scale because it is not completely soluble in water, and solids remain after thorough mixing. This issue was overcome by constructing a conical bottom tank with a bottom port to allow solids removal (**Figure 5.25**) and an engineered system with a jet pump to thoroughly mix the whey with injection water. However, when possible based on treatability studies, it is desirable to utilize a

completely soluble single chemical (e.g., acetate) as a cosubstrate rather than a complex mixture, such as cheese whey. The use of a single soluble substrate (1) simplifies the injection process, as the material can be metered into the groundwater from a drum or small tank; (2) allows both understanding and prediction of the routes of cosubstrate metabolism and the likely degradation intermediates; and (3) provides for better potential control of cosubstrate amount and groundwater ORP, as the stoichiometry of cosubstrate oxidation can easily be determined. In the case of the cheese whey product used, it was not possible to determine molar concentrations of the complex mixture (rather, TOC was used), and it is likely that some (or much) of the mixture was utilized by organisms other than those involved in explosives biodegradation, via fermentation and/or reduction of alternate electron acceptors such as manganese, sulfate, and iron. Thus, while the powdered cheese whey was extremely effective in promoting explosives biodegradation in this study, the application of a single, soluble substrate is desirable when possible based on the reasons stated above.

8.1.2 Technology Scale-up

Some reasonably large applications of this semi-passive approach have already been applied for contaminants other than nitroaromatic and nitramine explosives. For example, Krug and Cox, (2009) designed a system as a cut-off barrier for a 250-ft wide perchlorate plume emanating from a landfill at the Longhorn Army Ammunition Plant, that included a total of 13 extraction and injection wells. This system was operated with periodic manual injection of cosubstrate during pumping phases (3 weeks "on" and 8 months "off") which dramatically reduced costs. The system described herein at Picatinny Arsenal also was designed and built with all of the components required for application over a much larger plume area. The only changes required to utilize this system for a larger plume (as a cutoff barrier or source area treatment) would be the installation of additional extraction and/or injection wells, and the modification of piping runs to accommodate those extra wells. In this case, the system could be operated in an active mode at specific well loops (each consisting of 2 extraction wells and one injection well) at different times so that the only changes required during active operation at different well loops would be piping connections to the Conex box and cheese whey tank. Conversely, if long-term operation is anticipated, additional piping runs from the injection and extraction wells could be permanently added within the Conex box, and programmed for simultaneous extraction and injection during active cycles. Thus, all of the required components for a large-scale system are described in this document (see P&ID; **Figure 5.20**).

8.1.3 Secondary Impacts to the Local Aquifer

One of the typical benefits of active or semi-passive *in situ* treatment is a reduction in secondary groundwater impacts that are typical of passive approaches (e.g., vegetable oil injection), such as mobilization of dissolved iron and manganese, production and accumulation of methane gas, and generation of hydrogen sulfide. The injection and mixing of moderate amounts of cosubstrate into an aquifer, rather than quantities that are expected to persist for several years, minimizes the microbial reductive processes that cause the production of many of these secondary

contaminants. In a typical application, Fe an Mn will be mobilized within the treatment zone to mg/L concentrations, but these metals will be back to background levels within a several meters downgradient of the injection wells (Krug and Cox, 2009; Lippincott and Hatzinger, 2009). Similar results are expected for methane and hydrogen sulfide, each of which are quickly oxidized in an aerobic aquifer. It should also be noted, however, that the longer the interval between active cosubstrate addition phases, the higher the expected concentrations of secondary contaminants, such as dissolved Fe and Mn, within the aquifer. If shorter cycles are used, less cosubstrate can be injected at each cycle, and less excess will be available to promote biological reduction of sulfate, iron, manganese, etc.

During this demonstration, reasonably high concentrations of Fe, Mn, and methane were observed in some of the monitoring wells. For example, both Fe and Mn were detected at > 40 mg/L in 157MW-4 and 157MW-5, and methane exceeded 10 mg/L in 157MW-7S and 157MW-7D. Because this was largely a source zone treatment application, and groundwater transport was slow, it was not possible during the timeframe of the study to assess whether these compounds were still present in downgradient monitoring wells (i.e., the treated water did not reach downgradient wells 157MW-8S or 157MW-8D during the course of the study). However, one of the reasons for the relatively high concentration of these compounds during this study was the application of cheese whey rather than a single carbon substrate (as previously discussed in Section 8.1.2). In addition, relatively high concentrations of whey were added at each injection cycle so that the number of cycles could be minimized. This approach proved to be highly effective for remediation of explosives and degradation intermediates over the 565 day study, and no significant operational issues were experienced, such as well fouling. However, a trade-off for this approach was the production/mobilization of some secondary groundwater contaminants, such as Fe, Mn, and methane. Because there were no drinking wells in the local area and no close downgradient receptors, these contaminants were not deemed to be an important issue. However, mobilization of such contaminants should be considered in cases where downgradient receptors are present, and system operation and carbon sources should be chosen or adjusted accordingly.

8.1.4 Technology Cost Compared to Other Remedial Options

The expected cost drivers for the installation and operation of a semi-passive *in situ* bioremediation system for explosives and comparisons to other remedial approaches are provided in Section 7.

9.0. References

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APPENDIX A: Points of Contact

POINT OF CONTACT Name	ORGANIZATION Name Address	Phone/Fax/email	Role in Project
Paul B. Hatzinger	Shaw Environmental, Inc. 17 Princess Road Lawrenceville, NJ 08648	P: 609-895-5356 F: 609-895-1858 paul.hatzinger@shawgrp.com	Co-Principal Investigator
Charles E. Schaefer	Shaw Environmental, Inc. 17 Princess Road Lawrenceville, NJ 08648	P: 609-895-5372 F: 609-895-1858 charles.schaefer@shawgrp.com	Co-Principal Investigator
Pamela Sheehan	Building 355 US Army RDECOM-ARDEC Environmental Technology Division, EWETD Attn: AMSRD-AAR-AEE-E Picatinny Arsenal, NJ 07806	P: 732-310-0797 psheehan@eden.rutgers.edu	Co-Principal Investigator: Picatinny Arsenal

APPENDIX B: Quality Assurance Project Plan (QAPP)

Quality Assurance Project Plan (QAPP)

B.1 Purpose and Scope

This section presents the project-specific Quality Assurance Project Plan (QAPP) for ESTCP Project CU-0425, an *in situ* field demonstration of explosives bioremediation in Area 157 at Picatinny Arsenal. A cosubstrate (cheese whey) will be added to the Area 157 aquifer to stimulate naturally-occurring bacteria to degrade the explosives RDX, TNT, HMX, and various intermediate breakdown products of these compounds as specified in the workplan. This QAPP specifies the procedures the demonstration will follow to ensure it generates analytical data of known quality. These procedures are integral to the demonstration and complement the sampling procedures presented in Section 3 of the Workplan.

Both laboratory analytical and field screening methods will be used to measure parameters indicative of the demonstrations performance. The purpose of this QAPP is to outline steps to ensure that: (1) data generated during the course of the demonstration are of an acceptable and verifiable quality (*i.e.*, quality assurance); and (2) a sufficient number of control measurements are taken for proper data evaluation (*i.e.*, quality control).

B.2 Quality Assurance Responsibilities

Key QA personnel for the project and their responsibilities are outlined below.

Paul Hatzinger, Ph.D. is the Principal Investigator for the demonstration. He has overall project QA responsibility.

Randi Rothmel, Ph.D. is the Manager of Shaw's Analytical and Treatability Laboratory, and will have laboratory QA responsibility for anion (EPA Method 300.0) and TOC (EPA Method 415.1) analytical data during the project. In addition, Dr. Rothmel will perform external audits of the independent laboratories (Severn Trent Laboratories and ChemTech laboratories) conducting explosives analysis (EPA Method 8330) and Fe and Mn analysis (EPA Method 200.7). Dr. Rothmel will report directly to Dr. Hatzinger.

Pamela Sheehan, Ms. Sheehan will serve as the QA manager of the ETD Analytical lab at Picatinny Arsenal and will have QA/QC responsibility for all analytical data generated from this laboratory during the project.

Mr. Mark Magness located in Shaw's Mt. Arlington, NJ office, will serve as the project field manager. He will coordinate all field activities at Picatinny and will have overall QA responsibility for all field analyses. Mr. Magness will report to Dr. Hatzinger.

Mr. Kevin Gerdes located in Shaw's Mt. Arlington, NJ office, will assist with the coordination of field activities, including groundwater sampling. Mr. Gerdes will have day-to-day QA responsibility for field sampling and field analysis. Mr. Gerdes will report to Mr. Magness

B.3 Data Quality Parameters

This section describes all of the measurements that will be made to achieve the project's objectives.

The laboratory program for the biostimulation demonstration will include measuring the concentrations of explosives (TNT, RDX, HMX), anions (bromide, nitrate, sulfate, and chloride), total organic carbon (TOC), selected metals (iron and manganese), and other performance-related parameters (alkalinity, DO, redox) in groundwater monitoring well samples will also be measured. These measurements are outlined in Table 3.8 in the Workplan. Severn Trent Laboratories, Knoxville, TN will be used for explosives analysis via EPA Method 8330. Shaw's Analytical and Treatability Laboratory, Lawrenceville, NJ (New Jersey-certified, non-CLP) will be used for routine off-site analysis of anions and TOC. For all groundwater analyses, standard U.S. EPA methods will be used, as outlined in: (1) *U.S. EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods SW846*, Third Edition, revised November 1986, Update II, September 1994, Update IIB, January 1995, Update III, June 1997, Update IIIA, 1999, and Update IIIB, 2005; (2) *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater* (EPA-600/4-85 054, 1996); (3) *U.S. EPA Methods for Chemical Analysis of Water and Wastes* (EPA-600/4-79-020, 1983); (4) *Methods for Determination of Organic Compounds in Drinking Water* (EPA-600/4-88/039, 1998) and Supplement III, 1995; (5) *EPA Methods and Guidance for Analysis of Water, Version 2.0* (1999).

Additional groundwater parameters may be screened in the field using electronic meters. These parameters will be measured using methods approved or accepted by the U.S. EPA for reporting purposes. Groundwater field-measured parameters will include oxidation-reduction potential (ORP), pH, specific conductivity, dissolved oxygen (DO) and temperature.

B.4 Calibration Procedures, Quality Control Checks, and Corrective Action

B4.1 Quality Control Objectives

The goal of the biostimulation demonstration is to accomplish the following: 1) Evaluate the efficacy of the biostimulation technology with respect to explosives (TNT, RDX, HMX) degradation; 2) Develop the design criteria and protocol necessary for full-scale application of the technology; and 3) Evaluate the cost-effectiveness of the technology compared to existing explosives remediation technologies. As such, the project data quality objectives (Project DQOs) are as follows:

(1) collect data of sufficient quantity and quality to determine destruction efficiencies and biodegradation rates of explosives as a function of cosubstrate addition;

(2) collect data of sufficient quantity and quality to assess (a) site-specific biostimulation operating characteristics, (b) the extent of biostimulation operator attention required, and (c) the optimal range of biostimulation for treatment of groundwater at the demonstration site;

(3) collect data suitable for use in designing a full-scale biostimulation system; and

(4) collect data suitable for preparing a cost comparison analysis.

To meet the Project DQOs stated above, individual measurements must meet particular quantitative QA objectives for precision, accuracy, method detection limits, and completeness, as well as qualitative QA objectives for comparability and representativeness. This section describes the quality assurance objectives for the electron donor biostimulation demonstration in order to meet the specific Project DQOs stated above.

The specific data QA objectives are as follows:

- ♦ establish sample collection and preparation techniques that will yield results representative of the media and conditions analyzed;
- ♦ analyze method blanks, laboratory duplicates, matrix spikes, matrix spike duplicates, and surrogate spikes as required by the specific analytical methodology to determine if QA goals established for precision and accuracy are met for off-site laboratory analyses.

The data generated during the demonstration will be used primarily for assessing the efficacy of the electron donor biostimulation technology for remediating explosives contaminated groundwater. In an effort to produce data that will be useful for this assessment, definitions of data usage, data types, data acquisition, and data quality level have been made for each medium. These defined data parameters are collectively defined as DQOs. Table B.1 presents the DQOs for this technology demonstration. Table B.1 correlates data use with the required degree of analytical sophistication. This approach is based on the generalized DQOs presented by the USEPA, 1987. Five levels of data quality are used, ranging from Level I (field screening) to Level V (non-conventional methods). Due to the variation in the types of monitoring throughout the demonstration, data quality objective Levels I and III will be used. Several geochemical parameters, such as pH, temperature, and DO, will be determined in the field with immediate response required for process control (Level I). All off-site analytical laboratory measurements will be performed using Level III criteria for production of validated data.

Table B.1. Data Quality Objectives.

Environmental Media	Data Usage	Data Types	Data Acquisition	Data Quality/ Analytical level	Levels of Concern
Groundwater	Site Characterization	Define contamination in the test plot	Collect groundwater samples from the test plot; explosives and anion analysis	Laboratory analysis (Level III)	Limit of Detection
	Technology effectiveness	Determine effectiveness of technology for removal of the target compounds	Sample and analyze groundwater before, during and after field demonstration explosives, anions, metals, TOC analysis	Laboratory analysis (Level III)	Limit of Detection

Quality assurance objectives have been established to evaluate the criteria of precision, accuracy, and completeness. The evaluation of these criteria for validated (Level III) off-site laboratory analyses will be based upon matrix spikes, matrix spike duplicates, and surrogates, as described in Section B.4.3. Evaluation of method detection limits (MDLs) will be in accordance with each of the the methodological procedures cited in Table B.1

B.4.2 Analytical Procedures, and Calibration

Analytical Procedures. All laboratory analyses will be performed according to the established SW-846 and U.S. EPA Methods. Many of these methods are available at http://www.epa.gov/epaoswer/hazwaste/test/main.htm.

Calibration Procedures and Frequency. Calibration refers to the checking of physical measurements of both field and laboratory instruments against accepted standards. It also refers to determining the response function for an analytical instrument, which is the measured net signal as a function of the given analyte concentration. These determinations have a significant impact on data quality and will be performed regularly. In addition, preventative maintenance is important to the efficient collection of data. The calibration policies and procedures set forth will apply to all test and measuring equipment. For preventative maintenance purposes, critical spare parts will be obtained from the instrument manufacturer.

All field and laboratory instruments will be calibrated according to manufacturers' specifications. All laboratory instruments will be calibrated in accordance with established Standard Operating Procedures. Calibration will be performed prior to initial use and after periods of non-use. A record of calibration will be made in the field logbook each time a field instrument is calibrated. A separate logbook will be maintained by laboratory QA personnel similarly for laboratory instrumentation.

Process and Field Measurements. Field measurements will follow the guidelines specified in *Shaw's Addendum Laboratory SOP for Field Measurements of Analyze-Immediately Parameters* (2005). The portable instruments used to measure field parameters (*e.g.*, temperature, pH, etc.) will be calibrated in accordance with manufacturer's instructions. Flow measuring devices will not be calibrated if calibration requires the instruments to be sent back to the manufacturer. All other manufacturer-recommended checks of the flow instruments will be performed. The instruments will be calibrated at the start and completion of the demonstration. The pH, DO, and ORP probes will be calibrated prior to every site check during the demonstration.

Field Measurements: Groundwater. Groundwater will be assessed for dissolved oxygen, oxidation/reduction potential, conductivity, temperature, and pH. Depth to groundwater measurements will be taken using a water interface probe.

Dissolved Oxygen, Temperature, pH, Conductivity and Oxidation/Reduction Potential

Groundwater samples will be collected using a dedicated bladder pump connected to a surface compressor. The low flow collection protocol "Standard Operating Procedure for Low-Stress (low flow)/Minimal Drawdown Ground-Water Sample Collection" (Puls and Barcelona, 1996, EPA/540/S-95/504) will be used as a guideline for sampling. Samples will be measured for dissolved oxygen, temperature, pH, conductivity and redox potential under continuous flow using a multi-probe water quality meter (Horiba Model U-22, YSI probe, or similar). In order to minimize aeration of the sample, a continuous flow-through cell will be used to provide a sampling chamber for the meter. A sufficient volume of water from the well or groundwater sampling point will be purged before sample collection to ensure that a sample representative of the formation is obtained.

Depth to Groundwater

The depth to groundwater in site wells will be measured with a water interface probe (ORS Model #1068013 or equivalent). The probe lead is a 50- to 200-ft measuring tape with 0.01-ft increments. The

probe gives a constant beep when it encounters the water table. The water-level measurement will be recorded in the field logbook and the probe decontaminated between measurements.

Groundwater Sampling.

Prior to sampling, the well or sampling point identification will be checked and recorded along with the date and time in the field logbook. Groundwater samples will be collected using a bladder pump and flow-through cell as described previously. After the well is parameters are stabilized during low flow sampling to EPA method guidelines, two (2) 1L glass sample bottles without any chemical preservatives with Teflon-lined caps should be filled directly from the groundwater stream for analysis of explosives (EPA method 8330). The bottles should be completely filled to the neck, leaving a small headspace. The bottles should then be capped and placed on adequate ice for shipment. Next, one (1) 100-ml sample jar (glass or plastic, no chemical preservatives) should be filled to the top with water. The jar should then be capped and placed on ice for shipment. This sample will be used for analysis of anions by EPA Method 300 (nitrate, nitrite, sulfate, chloride, bromide). Next, one 40-mL glass VOA vial preserved with phosphoric acid should be filled to the top with water, capped, and placed on ice for shipment. This sample will be used for analysis of Total Organic Carbon (TOC) (EPA Method 415.1). Finally, at selected sampling points, a 500-ml amber glass jar preserved with nitric acid should be filled for analysis of total iron and manganese (EPA method 200.7). These analyses will be performed only during selected sampling events to evaluate mobilization of these metals in groundwater. Sample bottles for explosives analysis will be prepared by Severn Trent Laboratories, Knoxville, TN. Sample bottles for anions and metals will be prepared at the Shaw Environmental Laboratory in Lawrenceville, NJ. All sample bottles will be shipped to the Picatinny Site in an insulated cooler within 1 week prior to the scheduled sampling event.

Laboratory Measurements. The calibration procedures for all off-site analyses will follow the established SW-846 and U.S. EPA guidelines for the specific method. Certified standards will be used for all calibrations and calibration check measurements. The frequency and acceptance criteria for all off-site analyses will follow the guidelines outlined below.

Initial Calibration. During initial calibration, a minimum of one blank and five calibration standards that bracket the validated testing range will be analyzed singularly on one day. The concentration of the calibration standards will be prepared in the matrix that results from all the preparation steps of the method, taking into account any steps that are part of the method. Concentrations in the matrix will correspond to those in the environmental matrix as if the method preparation steps had been performed.

In addition to the initial calibration standards, the analysis of a calibration check standard is required prior to analysis of any samples. If the method requires what could be an initial calibration each day an analysis is performed, then the calibration check standards will be analyzed once each week rather than each day.

If the results of the calibration check standard are not acceptable, immediate re-analysis of the calibration check standard will be performed. If the results of the re-analysis still exceed the limits of acceptability, the system will be considered to have failed calibration. Sample analysis will be halted and will not resume until successful completion of initial calibration. Corrective actions taken to restore initial calibration will be documented in the analyst's notebook.

Daily Calibration. Calibration standards will be analyzed each day analyses are performed to verify that instrument response has not changed from previous calibration. Each day before sample analysis, a mid-

range concentration standard will be analyzed. The response must fall within the required percentage or two standard deviations of the mean response for the same concentration, as determined from prior initial/daily calibrations (see below). If the response fails this test, the daily standard will be re-analyzed. If the response from the second analysis fails this range, initial calibration will be performed before analyzing samples.

Each day after sample analyses are completed, a second standard will be analyzed. If the response is not within the required percentage or two standard deviations of the mean response from prior initial/daily calibrations, the daily standard will be re-analyzed. If the response from the second analysis fails this range, the system will be considered to have failed calibration. Initial calibration will then be performed and all samples re-analyzed since the last acceptable calibration will be re-analyzed.

For non-linear or non-zero-intercept calibration curves, daily calibration will consist of analysis of the low, middle, and high standards at the beginning of the day. When sample analyses are completed at the end of the day, the low and high standards will be analyzed. Instrument responses for each concentration determination must fall within two standard deviations of the mean response, as described previously, for the appropriate standard. For calibrations fitted by the quadratic equation, a minimum of four standards over the validated range are required, along with the highest level standard analyzed at the end of the day. For all other equations, one more standard than needed to meet the degrees of freedom for any lack-of-fit is required, as a minimum.

Calibration Check Standards. Calibration check standards will be analyzed during each initial calibration. The calibration check standard will contain all analytes of interest for the method in question at a concentration as required by the method. Results of the calibration check standards must fall within the limits of acceptability as described below:

Case 1 - A certified check standard is available from the U.S. EPA or some other source with both the true value and limits of acceptability specified by the supplier. The results must fall within the limits specified by the supplier, or ± 20% for inorganics and ± 15% for organics, whichever is less.

Case 2 - A certified check standard is available from the U.S. EPA or some other source with a true value specified but without limits of acceptability. The results must fall within ± 20% for inorganics and within ± 15% for organics.

Case 3 - If no certified check standard is available, the laboratory shall prepare a check standard using a second source of reference material. This standard shall be prepared by a different analyst than the one who prepared the calibration standard. If weighing of the material is required, a different balance will be used, if possible. The results must fall within ± 20% for inorganics and within ± 15% for organics.

Case 4 - If there is only one source of reference material available, then the calibration and calibration check standards must be prepared from the same source. The standards shall be prepared by different analysts. If weighing is required, different balances will be used, if possible. The results must fall within ± 20% for inorganics and within ± 15% for organics.

For all cases listed above, after the seventh acceptable check standard, the limits of acceptability will be ± two standard deviations, as determined from the first seven points.

For multi-analyte methods, the calibration check standard will contain all analytes of interest (target analytes). For the check standard to be deemed acceptable, at least two-thirds of the analytes must meet the limits of acceptability as defined above. In addition, if a single target analyte falls outside the limits of acceptability for two consecutive times, then the calibration check standard will be deemed unacceptable. If a calibration check standard is not acceptable, the procedures detailed above will be followed.

B.4.3 Internal Quality Control Checks

Quality Control Samples. Internal QC data provides information for identifying and defining qualitative and quantitative limitations associated with measurement data. Analysis of the following types of QC samples will provide the primary basis for quantitative evaluation of analytical measurement data quality:

Field QC Samples

- equipment blanks to evaluate the potential for contamination from ambient conditions, sampling equipment, or sample collection techniques. This chance is minimized by using dedicated sampling pumps in each well, so these blanks are not required.

Laboratory QC Samples

- method blanks, laboratory duplicates, matrix spikes, and matrix spike duplicates to determine if QA goals established for precision and accuracy are met by the analytical laboratory.

The number, type, and frequency of laboratory QC samples will be dictated by the validated SW-846 or U.S. EPA Methods used by the Shaw E&I laboratory and by the off-site laboratories. The SW-846 and U.S. EPA Methods specify the number and types of laboratory QC samples required during routine analysis. This information will be supplied with the data package provided by the laboratory.

In addition to the internal QC samples described above, the off-site laboratories will provide, at a minimum, additional internal QC checks as follows:

- use of standard analytical reference materials for traceability of independent stock solutions prepared for calibration stocks, control spike stocks, and reference stock solutions;
- verification of initial calibration curves with independent reference stock solutions according to Section B.4.2;
- verification of initial calibration curves with daily calibration standards according to Section B.4.2;
- verification of continued calibration control by analysis of calibration standards to document calibration drift;
- analysis of control spikes to document method performance and control with respect to recent performance.

An attempt will be made to analyze all samples within the calibrated range of the analytical method. Dilution of a sample extract with extracting solvent, or of the original sample matrix with distilled/de-ionized water, will be performed if the concentration of an analyte is greater than the calibrated range of the method.

Blank Samples

Blanks are artificial samples designed to detect the introduction of contamination or other artifacts into the sampling, handling, and analytical process. Blanks are the primary QC check of measurements for trace-level concentrations.

Equipment Blanks. Equipment blanks are used to assess the level of contamination of sampling devices. Groundwater samples will be collected using a bladder pump with dedicated polyethylene tubing. Because the pumps and tubing are dedicated in each well, and because a low flow sampling procedure is used in which parameters must stabilize prior to sample collection (i.e., water is flowing continually through the flow cells), equipment blanks will not be taken during this project.

Method Blanks. Method blanks will be prepared by the off-site laboratories to evaluate the impact of the analytical process on detected concentrations of contaminants. Method blanks will be prepared for each batch of samples run for a given method of analysis. The method blanks will be processed through the entire preparation and analytical procedure in the same manner as field samples. The method blanks will provide data to assess potential systematic contamination of the measurement system.

Laboratory Control Samples. Laboratory control samples will be used by the laboratory to assess analytical performance under a given set of standard conditions. These samples will be specifically prepared to contain some or all of the analytes of interest at known concentrations. The samples will be prepared independently of the calibration standards. Types of laboratory control samples that may be used are laboratory duplicates, matrix spikes, matrix spike duplicates, and surrogate spikes. Analysis of laboratory control samples will be used to estimate the analytical bias and accuracy by comparing measured results obtained during analysis to theoretical concentrations. This comparison will be measured using Equation B.1 as presented in Section B.5. The matrix spike/matrix spike duplicate samples will be used to evaluate precision according to Equation B.2. The accepted range of RPD values for *matrix spike/matrix spike duplicate* samples for each laboratory analysis will be in accordance with the Methods presented in Appendix B. Stock solutions used to spike QC samples will be prepared independently of stocks used for calibration as required by appropriate EPA methods. Validation of spiked solutions will be performed on a regular basis before the solution is used.

B.4.4 Sample Documentation

The on-site Field Engineer will coordinate with the off-site laboratories for shipment and receipt of sample bottle, coolers, icepacks, chain-of-custody (COC) forms, and Custody Seals. Upon completion of sampling, the COC will be filled out and shipped with the samples to the laboratory. An important consideration for the collection of environmental data is the ability to demonstrate that the analytical samples have been obtained from predetermined locations and that they have reached the laboratory without alteration. Evidence of collection, shipment, laboratory receipt, and laboratory custody until disposal must be documented to accomplish this. Documentation will be accomplished through a COC

Record that records each sample and the names of the individuals responsible for sample collection, transport, and receipt. A sample is considered in custody if it is:

- in a person's actual possession;
- in view after being in physical possession;
- sealed so that no one can tamper with it after having been in physical custody; or
- in a secured area, restricted to authorized personnel.

Sample custody will be initiated by field personnel upon collection of samples. As discussed in Section 3, samples will be packaged to prevent breakage or leakage during transport, and will be shipped to the laboratory via commercial carrier, or transported via car or truck.

Sample Identification. A discrete sample identification number will be assigned to each sample. These discrete sample numbers will be placed on each bottle and will be recorded, along with other pertinent data in a field notebook dedicated to the project. For blind samples, the sample location will be recorded in the field notebook along with a note indicating that the sample was submitted to the laboratory as a blind sample. The sample identification number will designate the sample location ("157MW-" for specific monitoring well) and date collected. For example, a sample collected from the 157MW-4 groundwater sample port collected November 22, 2005 would be identified as follows:

157MW-4-11/22/05

Chain-of Custody Forms. The COC Record used by Shaw's laboratory is shown in Figure B.1. This COC form will be supplied with sample bottles that are shipped to the site. All samples collected for off-site analysis will be physically inspected by the Field Engineer prior to shipment.

Each individual who has the sample in their possession will sign the COC Record. Preparation of the COC Record will be as follows:

- The COC Record will be initiated in the field by the person collecting the sample, for every sample. Every sample shall be assigned a unique identification number that is entered on the COC Record.
- The record will be completed in the field to indicate project, sampling person, etc.
- If the person collecting the samples does not transport the samples to the laboratory or ship the samples directly, the first block for "Relinquished By _____, Received By _____" will be completed in the field.
- The person transporting the samples to the laboratory or delivering them for shipment will sign the record for as "Relinquished By _____".
- The original COC Record will be sealed in a watertight container, taped to the top (inside) of the shipping container, and the shipping container sealed prior to being given to the commercial carrier. A copy of the COC Record will be kept on-site.
- If shipping by commercial carrier, the waybill will serve as an extension of the COC Record between the final field custodian and receipt by the off-site laboratory.

- Upon receipt by the off-site laboratory, the laboratory QC Coordinator, or designated representative, shall open the shipping container(s), compare the contents with the COC Record, and sign and date the record. Any discrepancies shall be noted on the COC Record.
- The COC Record is completed after sample disposal.
- COC Records will be maintained with the records for the project, and become part of the data package.

17 Princess Road
Lawrenceville, NJ 08648
609-936-9300/ 609-936-9221
Shaw Environmental and Infrastructure Inc.

CHAIN OF CUSTODY

Ref. Document # _____

Page _____ of ___

Project Number/Cost code: _____ /

Project Name / Location: _____ /

Purchase Order #: _____

Project Contact: _____
(Name & phone #)

Shipment Date: _____

Waybill/Airbill Number: _____

Lab Destination: _____

Lab Contact Name / ph. #: _____

Send Report To: _____

Phone/Fax Number: _____

Address: _____

City/State: _____

Sampler's Name(s): _____

Lab No.	Sample ID Number	Sample Description	Collection Information: Date	Time	G/C	Matrix	# of containers	Container type	Preservative: HCL	NaOH	HNO_3	H_2SO_4	Ice	Analyses Requested	Turn Around Time Requested

Special Instructions:

Known Waste Stream Circle:
RCRA PCB/dioxin PAH/oil RAD Corrosive Flammable Reactive

QC/Data Package Level Required:
I II III IV NJ EDD GIS EDD Preliminary data

Relinquished By: Date: Time:

Received By: Date: Time:

Relinquished By: Date: Time:

Received By: Date: Time:

Relinquished By: Date: Time:

Received By: Date: Time:

G/C Codes
C = Composite G = Grab

QC Package Codes
Level I = data summary
Level II = data summary + basic QC
Level III = New Jersey QC reduced deliverable
Level IV = Full deliverable CLP package

Cooler temperature upon arrival at Lab:

Figure B.1. Shaw Chain of Custody Form.

Laboratory Sample Receipt. Following sample receipt, the Laboratory Manager will:

- Examine all samples and determine if proper temperature has been maintained during transport. If samples have been damaged during transport, the remaining samples will be carefully examined to determine whether they were affected. Any samples affected shall be considered damaged. It will be noted on the COC Record that specific samples were damaged and that the samples were removed from the sampling program. Field personnel will be instructed to re-sample, if appropriate.
- Compare samples received against those listed on the COC Record.
- Verify that sample holding times have not been exceeded.
- Sign and date the COC Record, attaching the waybill if samples were shipped for off-site analysis.
- Denote the samples in the laboratory sample log-in book which will contain, at a minimum, the following information:

    - Project Identification Number
    - Sample numbers
    - Type of samples
    - Date and time received

- Place the completed COC Record in the project file.

The date and time the samples are logged in by the Sample Custodian or designee should agree with the date and time recorded by the person relinquishing the samples. Any nonconformance to the stated procedures that may affect the cost or data quality should be reported to the Principal Investigator.

Other Documentation. Following sample receipt at the laboratory, the Laboratory Manager or sample custodian will clearly document the processing steps that are applied to the sample. The analytical data from laboratory QC samples will be identified with each batch of related samples. The laboratory log book will include the time, date, and name of the person who logged each sample into the laboratory system. This documentation will be thorough enough to allow tracking of the sample analytical history without aid from the analyst. At a minimum, laboratory documentation procedures will provide the following:

- Recording in a clear, comprehensive manner using indelible ink;
- Corrections to data and logbooks made by drawing a single line through the error and initialing and dating the correction;
- Consistency before release of analytical results by assembling and cross-checking the information on the sample tags, custody records, bench sheets, personal and instrument logs, and other relevant data to verify that data pertaining to each sample are consistent throughout the record;

- Observations and results identified with the project number, date, and analyst and reviewer signatures on each line, page, or book as appropriate;
- Data recorded in bound books or sheaf of numbered pages, instrument tracings or hard copy, or computer hard copy; and,
- Data tracking through document consolidation and project inventory of accountable documents: sample logbook, analysis data book, daily journal, instrument logbook, narrative and numerical final reports, etc.

B.4.5 Data Reduction, Validation, and Reporting

This section describes procedures for reducing, validating, and reporting data. All validated analytical data generated within the off-site laboratories will be extensively checked for accuracy and completeness by laboratory and project personnel. Records will be kept throughout the analytical process, during data generation, and during reporting so that adequate documentation to support all measurements is available. Recordkeeping, data reduction, validation, and reporting procedures are discussed in this section.

Data Reduction. Data reduction will follow the requirements contained in the SW-846 and USEPA analytical methods cited previously. Reduction involves the reformatting of data to present the desired end-product, *i.e.*, the concentrations of the contaminants. Reformatting will involve the process of performing calculations on the raw data and presenting all values in appropriate units. The information generated by the data reduction step will be used in the interpretation of the data qualifiers.

The responsibility for data acquisition and reduction of raw data resides with the analysts who perform the analysis. Raw data for the quantitative 8330 analysis (explosives) procedure used during this project will consist of peak areas for surrogates, standards, and target compounds by HPLC. Analytical results will be reduced to concentration units appropriate for the medium being analyzed, i.e. micrograms per liter (μg/L) for aqueous samples.

Data Validation. Data validation involves a review of the QC data and the raw data in order to identify any qualitative, unreliable, or invalid measurements. As a result, it will be possible to determine which samples, if any, are related to out-of-control QC samples. Laboratory data will be screened for inclusion of and frequency of the necessary QC supporting information, such as detection limit verification, initial calibration, continuing calibration, duplicates, matrix spikes, surrogate spikes, and the method and preparation blanks. QC supporting information will be screened to determine whether any datum is outside established control limits. If out-of-control data are discovered, appropriate corrective action will be determined based upon QC criteria for precision, accuracy, and completeness. Any out-of-control data without appropriate corrective action will be cause to qualify the affected measurement data.

Levels of data validation for the demonstration are defined below:

- **Level I.** For Level I field screening data quality, a data "package" including the results from sample blanks, method blanks, and supporting calibration information, will be recorded in the field logbook and on log sheets maintained within a folder on-site. The extent of contamination and the achievement of detection limits can be determined from this information. The sample results and QC parameters will be routinely evaluated by site personnel, and 10% of the analytical raw data results will be reviewed by the Project Manager (Dr. Paul Hatzinger) to verify sample

identity, instrument calibration, quantification limits, numerical computation, accuracy of transcriptions, and calculations.

- **Level III.** For Level III validated data quality, a CLP-like data package will be provided. For the SWB8330 explosives analyses, this includes CLP-like summary forms 1 through 10 and all raw data associated with the samples, without the chromatograms of calibration standards, matrix spikes, or matrix spike duplicates. The laboratory deliverable format for the New Jersey-certified laboratories will follow the guidelines in Appendix A "Laboratory Data Deliverables Formats - Section III (Reduced Laboratory Data Deliverables - USEPA/CLP Methods)" CITE 25 of the New Jersey Register (NJR), February 3, 2003. Sample results will be evaluated according to the current version of the U.S. EPA functional guidelines for organic and inorganic analyses for selected QA/QC parameters, and 10% of the analytical raw data results will be reviewed to verify sample identity, instrument calibration, detection limits, numerical computation, accuracy of transcriptions, and calculations.

At a minimum, the following data validation procedures will be followed.

Each data package will be reviewed and the data validated prior to submission. Checklists will be used to demonstrate that the data review was accomplished. The Laboratory Manager or designee will perform the data review and validation.

The data review will include, but not be limited to, the following subjects:

- Completeness of laboratory data;
- Evaluation of data with respect to reporting limits;
- Evaluation of data with respect to control limits;
- Review of holding time data;
- Review of sample handling;
- Correlation of laboratory data from related laboratory tests;
- Comparison of the quality of the data generated with DQOs as stated in this Work Plan (on a daily basis, during routine analyses, and during internal laboratory audits); and
- QC chart review, performed yearly. Review shall consist of assessing trends, cycles, patterns, etc. This review shall also assess whether control corrective actions have been implemented.

The elements of data validation shall include, but not be limited to, the following items:

- Examination of COC records to assess whether custody was properly maintained;
- Comparison of data on instrument printouts with data recorded on worksheets or in notebooks;
- Comparison of calibration and analysis dates and assessment of whether the same calibration was used for all samples within a lot;
- Comparison of standard, sample preparation, and injection records with instrument output to assess whether each output is associated with the correct sample;
- Examination of calibration requirements, as specified in the methods;

- Use of a hand-held calculator to perform all calculations on selected samples to assess the correctness of results; and
- Examination of all papers and notebooks to ensure that all pages are signed and dated, that all changes are initialed, dated, have sufficient explanation for the change, and that all items are legible.

Required record-keeping following a laboratory audit shall document that all lots were reviewed in the audit report. The audit report shall also identify any deficiencies that were noted. A copy of the audit report shall be placed in the applicable installation audit folder.

Data Reporting. Data and information generated during the demonstration will be summarized in a Technology Application Analysis Report, to be submitted at the completion of the project. QA/QC analysis reports will be generated by laboratory personnel as a product of validation procedures described above. All off-site Level III analyses will be accompanied by QA/QC data packages as described in the previous section. The summary QA/QC reports will not be included in the Technology Application Analysis Report, but will be made available upon request. The ultimate data set produced for project use will consist of all values reported in appropriate units flagged with respective data qualifiers for entry into the project database as described below. Analytical results will be reduced to concentration units appropriate for the medium being analyzed:

- "μg/L" or "mg/L", depending on analyte and method, for aqueous samples.

The laboratory will retain all samples and sample extracts for 6 weeks following data package submittal.

The results for each analyte in spiked QC samples will be determined using the same acceptable calibration curve that is used for environmental samples in the lot. Values above the practical quantitation limit (PQL) shall be reported as the found value. Raw values that fall below the method detection limit (MDL) will be reported as "less than" the PQL. Values above the method detection limit (MDL) and less than the PQL will be reported and flagged with a "J Results for QC samples will not be corrected, except as described below. Because all spike levels must be within the calibrated range, no dilutions should be required. Data will be reported using the correct number of significant figures.

Each day of analysis, the analyst will quantify each analyte in the method blank and spiked QC samples. Data from the method blank will be reported, usually as less than the PQL for each analyte. Any values above the PQL shall be reported as the found value. Corrections to the QC samples, necessitated by background levels in the method blank, will be performed using instrument response values and not the found values calculated from the linear calibration curve. Reported entries will be in terms of concentration. The importance attached to finding measurable concentrations in the method blank is dependent on analyte and method. Identification of measurable concentrations in the method blanks will be reported in writing to the Principal Investigator for possible corrective actions.

The following additional data reporting procedures will be followed.

All data will be reported, and numerical results will be reported in terms of concentration in the environmental sample. Resultant found concentrations will be adjusted for dilution, etc. before being reported, and both the raw data and correction factors (*e.g.*, percent moisture, and dilution factor) will be

recorded in the data package submitted. Laboratory comments on the usability of the data will also be included.

In reporting results, rounding to the correct number of significant figures will occur only after all calculations and manipulations have been completed. As many figures as are warranted by each analytical technique will be used in pre-reporting calculations. Rounding will be accomplished using the following rules:

Rule 1 - In expressing an experimental quantity, retain no digits beyond the second uncertain one.

Rule 2 - In rounding numbers (*i.e.*, in dropping superfluous digits):

- Increase the last retained digit by one if the first uncertain digit is larger than 5;
- Retain the last digit unchanged if the first uncertain digit is less than 5;
- Retain the last digit unchanged if even, or increase it by one if odd, if the first uncertain digit is 5 and the second uncertain digit is 0;
- Increase the last retained digit by one if the first uncertain digit is 5 and the second uncertain digit is greater than 0.

The correct number of reported significant figures, by validation type, is 3 significant figures. The number of allowable significant figures is reduced when added uncertainties are included in the analysis, *i.e.*, the results for samples diluted into the validated range allow one less significant figure due to the uncertainty added by the dilution process.

B.4.6 Corrective Action Plan

If routine procedures (*e.g.*, equipment calibration), QC sample analysis, or performance and system audits indicate that sampling or analysis systems are unsatisfactory, a corrective action shall be implemented. If previously reported data are affected by the situation requiring correction or if the corrective action will impact the project budget or schedule, the action will directly involve the Principal Investigator. ESTCP will be informed of all major performance problems, and will be included in corrective action planning.

Corrective actions are of two kinds:

1. Immediate, to correct or repair non-conforming equipment and systems. The need for such an action will most frequently be identified by the analyst or technician as a result of calibration checks and QC sample analyses. Immediate corrective actions address problems peculiar to a single measurement or lot of samples. Immediate corrective action may include:

    - Re-run of analyses if sample holding times have not been exceeded;
    - Instrument re-calibration using freshly prepared standards;
    - Replacement of reagents or solvents that give unacceptable blank values;
    - Examination of data calculation errors; and
    - Replacement of reference standards that have been degraded.

If corrective action indicates that non-conformance is due to problems with laboratory equipment, procedures, and/or calibration, once the problem is resolved, the non-conforming samples will be re-analyzed if holding times have not been exceeded. If holding times have been exceeded, new samples will be collected if the completeness criteria specified in Section B.5 require that these samples be collected. If corrective action indicates that non-conformance of duplicate samples is due to sampling technique, once the problem is corrected, new samples will be collected if the completeness criteria specified in Section B.5 requires that these samples be collected.

2. Long-term, to eliminate causes of non-conformance. The need for such actions will probably be identified by audits. Long-term corrective actions may address procedural deficiencies or unsatisfactory trends or cycles in data that affect multiple lots of samples. Examples of long-term corrective action may include:

    - Staff training in technical skills or in implementing the QAPP;
    - Rescheduling of laboratory routine to ensure analysis within allowed holding times;
    - Identifying alternate vendors to supply reagents of sufficient purity; and
    - Revision of the QAPP.

For either immediate or long-term corrective action, steps comprising a closed-loop corrective action system will be implemented as follows:

- Define the problem;
- Assign responsibility for investigating the problem;
- Investigate and determine the cause of the problem;
- Determine a corrective action to eliminate the problem;
- Assign responsibility for implementing the corrective action; and
- Verify that the corrective action has eliminated the problem.

Unsatisfactory items or situations may be identified by anyone involved with the project, particularly the analysts, field engineers, technicians, or QA personnel. Depending on the nature of the problem, the corrective action employed may be formal or informal.

To enhance the timeliness of corrective action and thereby reduce the generation of unacceptable data, problems identified by assessment procedures will be resolved at the lowest possible management level. Problems that cannot be resolved at this level will be reported to the Project Manager. The Project Manager will determine the management level at which the problem can best be resolved, and will notify the appropriate manager. Monthly progress reports from the on-site Field Engineer will detail all problems and subsequent resolutions.

In all cases, the occurrence of the problem, the corrective action(s) employed, and verification that the problem has been eliminated will be documented. In addition, if the corrective action results in the preparation of a new standard or calibration solution(s), then a comparison of the new versus the old standard or solution will be performed, and the results supplied with a full QC report as verification that

the problem has been eliminated. Corrective action reports that relate to a particular lot analysis will be included in the data package for that lot.

B.5 Calculation of Data Quality Indicators

B.5.1 Quantitative QA Objectives: Accuracy, Precision, Completeness, and Method-Detection Limit

Accuracy: Accuracy indicates the degree of bias in a measurement system, and is the degree of agreement of a measurement with an accepted reference value. Sample measurement uses laboratory equipment. The percent recovery of matrix spike/matrix spike duplicate samples measures the accuracy of the laboratory equipment, calculated according to the following equation:

$$\%R = (C_I - C_o)/ C_t * 100 \qquad \text{(Equation B.1)}$$

Where: %R = percent recovery
C_I = measured concentration; spiked sample aliquot
C_o = measured concentration, unspiked sample aliquot
C_t = actual concentration of spike added

Precision: Precision is the reproducibility of measurements under a given set of conditions. For large data sets, precision is expressed as the variability of a group of measurements compared to their average value. Variability may be attributable to field practices or chemical analyses. Precision is expressed as relative percentage difference, determined using Equation B.2 below.

Precision is measured by calculating the Relative Percent Difference (RPD) of laboratory duplicates, matrix spike/matrix spike duplicate sample pairs, surrogate spikes, and field duplicate samples.

$$RPD = (C_1 – C_2) *100/ ((C_1 + C_2)/2) \qquad \text{(Equation B.2)}$$

Where: RPD = relative percent difference
C_1 = the larger of the two observed values
C_2 = the smaller of the two observed values

Completeness: Completeness is defined as the qualified and estimated results, and represents the results usable for data interpretation and decision making. Results qualified as rejected or unusable, or that were not reported because of sample loss, breakage, or analytical error, negatively influence completeness and are subtracted from the total number of results to calculate completeness. Percent completeness is determined by using the following equation:

$$\% \text{ Completeness} = (VDP/ TDP) * 100 \qquad \text{(Equation B.3)}$$

Where: VDP = number of valid data points
TDP = number of total samples obtained

Completeness will be calculated for each method and matrix during the demonstration. The completeness objective for all validated data is 95 percent.

Method-Detection Limits. Method detection limits (MDLs) and practical quantitation limits (PQLs) must be distinguished for proper understanding and data use. The MDL is the minimum analyte concentration that can be measured and reported with a 99% confidence that the concentration is greater than zero. The PQL represents the concentration of an analyte that can be routinely measured in the sampled matrix with "reasonable" confidence in both identification and quantitation. PQLs are often based on analytical judgement and experience, and should be verifiable by having the lowest non-zero calibration standard or calibration check sample concentration at or near the PQL. Table B.2 presents the MDL range and PQLs for the analytical methods to be used during the demonstration. The limits shown in Table B.2 assume optimal conditions. MDLs may be higher, particularly in contaminant mixtures, due to dilution limits required for analysis. Concentrations detected below the PQL will be appropriately flagged. These flagged concentrations will be considered below the practical quantification limits of the analytical method used, but will not negatively impact completeness.

The evaluation of method detection limits (MDLs) will be in accordance with the procedures outlined in Appendix B to Part 136 "Definition and Procedures for the Determination of Method Detection Limit - Revision 1.1," 40 Code of Federal Regulations (CFR) 136, 1984. Method quantification limits and detection limits will be reported for each sample set of validated data. The calculated MDL shall be equal to or less than the Required Detection Level (RDL). If the calculated MDL is lower than the level the laboratory deems practical, the calculated MDL may be raised to a higher level. In no instance shall the reported MDL be below the calculated level. The method documentation shall include both the calculated MDL and the request for an increased reportable MDL. Raising the reportable MDL to a higher level will be contingent upon approval by Shaw's Principal Investigator and ESTCP.

Table B.2. Range of Method Detection Limits and Quantitation Limits for Analytical Methods Used During the Field Demonstration.

Sample Matrix	Analysis	Method	Reporting Method Detection Limits	Quantitation Limits
Groundwater	Explosives	8330.0	0.05 - 0.12 ug/L	0.2 - 0.5 ug/L*
	TOC	415.1	0.17 mg/L	1.0 mg/L**
	Metals (Fe, Mn)	200.7	0.05, 0.01 mg/L	0.05, 0.01 mg/L***
	Anions (NO_3^-, NO_2^-, SO_4^-, Br^-,Cl^-,PO_4^-)	300.0	0.01-0.03 mg/L	0.05, 0.01 mg/L**

Notes:
Explosives = TNT, RDX, HMX, and breakdown products as specified in 8330
Mn = dissolved manganese
Fe = dissolved iron
NO_3^- - Nitrate
NO_2^- - Nitrite
SO_4^- - Sulfate
Br^- - Bromide
Cl^- - Chloride
TOC - Total Organic Carbon

* Values from STL Knoxville, TN Laboratory
** Values from Shaw ATL, Lawrenceville, NJ
*** Values from ChemTech Labs, Mountainside, NJ

B.5.2 Qualitative QA Objectives: Comparability and Representativeness

Comparability refers to the confidence with which one data set can be compared to another. Comparability is essential for the evaluation of technology performance compared to that of similar technologies. Comparable data will be generated by following standard SW-846 and U.S. EPA protocols for all laboratory analyses, and manufacturers' instructions for all on-site test kits and meters.

Representativeness is a measure of the degree to which data accurately and precisely represent the conditions of the parameter represented by the data. Collected samples must be representative of the matrix characteristics and contamination concentrations. Representativeness is affected by errors introduced through the sampling process, field contamination, preservation, handling, sample preparation, and analysis.

Representativeness will be ensured through the following practices:

- selecting the necessary number of samples, sample locations, and sampling procedures that will depict as accurately and precisely as possible the matrix and conditions measured;
- developing protocols for storage, preservation, and transport that preserve the representativeness of the collected samples;
- using documentation methods to ensure that protocols have been followed and that samples are properly identified to maintain integrity and traceability; and
- using standard, well-documented analytical procedures to ensure consistent, representative data.

B.6 Data Storage and Archiving Procedures

All raw data, documentation, records, test plans, analyses, reports and correspondence generated as a result of this demonstration will be properly stored and archived in paper and electronic file formats as appropriate. Project data and analyses will be stored in an organized fashion to facilitate retrieval in an expedient fashion. Paper files will be maintained and stored so as to minimize deterioration during and after the project is complete. Electronic files associated with the project will be automatically backed-up on a monthly basis during the active phase of the project. Electronic files will be archived on CD-ROM or tape backup upon completion of the project to ensure data integrity.

APPENDIX C: Fate and Transport Model for Conceptual Design

Fate and Transport Model for Conceptual System Design

The hydraulic conceptual model was constructed using MODFLOW. The MODFLOW model was used to simulate subsurface groundwater flow in the test area due to natural hydraulic gradients and operation of the injection and extraction wells. The details of model conceptual design are summarized in Table C-1 (following this text) The model consisted of 4 grid layers, with each layer representing approximately 27 ft in thickness (108 feet total model aquifer depth). The simulated area of each grid ranged from 63 ft^2 along the edges to 9 ft^2 in the center of the model domain within the actual simulated test plot. The total area of the model domain was approximately 69,972 ft^2 (294 ft x 238 ft). The critical assumptions and parameters used in the development of the MODFLOW hydraulic model were as follows:

- The simulated horizontal hydraulic conductivity was 26 ft/day, which was based on the value obtained during the slug testing (Section 5.2.4). The assumed ratio of horizontal to vertical hydraulic conductivity was 3.

- Based on measured hydraulic conductivities and hydraulic gradients, and assuming a porosity of 0.3, the simulated groundwater flow rate within the demonstration area (top to bottom in Figures 5.17,b and 5.18a,b) was approximately 0.01 ft/day.

- Simulated extraction wells were placed 48 feet apart, with the simulated injection well placed between them but 7 feet upgradient. Extraction and injection wells were aligned perpendicular to groundwater flow. Simulated extraction and injection well flow rates were 5 gpm and 10 gpm, respectively.

- Simulated injection and extraction wells were screened through the top 25 ft. of the saturated zone.

MODFLOW simulations were performed under transient conditions to simulate cycled pumping and recirculation of the treatment system. A cycle of three days “on” (5 gpm at each extraction well and 10 gpm at the injection well) and 15 days “off” was simulated for a 6-month Period of Operation.

Solute fate and transport was simulated using SEAM3D, which interfaces with the MODFLOW hydraulic model. Specific constituents simulated in the SEAM3D model include TNT, RDX, HMX, cosubstrate (cheese whey), and bromide. Key model assumptions and input parameters were as follows:

- The porosity was estimated at 0.3.

- The longitudinal dispersivity was estimated at 1.0 ft.

- Background TNT, RDX, and HMX concentrations were 40 µg/L, 70 µg/L, and 80 µg/L, respectively.

- Biodegradation of TNT, RDX, and HMX were simulated using first order degradation kinetics. Simulated biodegradation rate constants, based on measured values obtained in the laboratory microcosm studies, were 0.46/day, 0.030/day, and 0.011/day for TNT, RDX, and HMX (respectively).

- Sorption was assumed to be negligible.

- Simulated bromide injection concentration was 200 mg/L; simulated electron donor (cheese whey) injections were 500 mg/L.

The SEAM3D model was run for 180 days to evaluate the impacts of electron donor addition on target contaminants within and downgradient of the test area.

It should be noted that the simulated contaminant concentrations injected into the injection well were assumed to remain constant at values equal to half of their initial background levels. In reality, the concentrations of these compounds re-injected from the extraction wells will decrease with time as groundwater within the capture zone of the extraction wells begins to become depleted in electron acceptor concentrations. In addition, simulation results show that TNT and RDX concentrations at the simulated extraction wells are all less than 1 µg/L by the end of the 180-day simulation. Thus, in reality, the concentration of contaminants in the re-circulated groundwater will be less than what is currently simulated in the models and contaminant removal is expected to be more rapid than what is shown in the simulations (Figures 5.17,b and 5.18a,b).

Table C-1. Details of Model Conceptual Design.

Model Component	Number of locations	Flow rate (gpm)	Screen Length (ft)	Concentration (mg/L)
Injection Well	1	10	25	NA
Extraction well	2	5	25	NA
Cheese Whey (electron donor)	1	*at injection well*	NA	500
Bromide	1	*at injection well*	NA	200

NA = Not applicable